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Abstract

Biofouling is a major problem during microfiltration that causes a reduction in filtration flux and an alteration in membrane selectivity over time. Mathematical modeling of fouling behavior plays an important role in the understanding of complex fouling mechanisms. There is growing interest in the use of both asymmetric and composite membranes for microfiltration and ultrafiltration processes. Previous studies indicate that different asymmetric membrane structure has a significant impact on both filtration flux and sieving property. However, most of previous fouling models were developed for homogeneous membranes. The effects of asymmetric membrane structure on fouling behavior remains poorly understood on a fundamental level.

A three-mechanism model was first developed to account for both external fouling and internal fouling by combining three classical fouling mechanisms: pore blockage, pore constriction, and cake filtration. Based on this combined fouling model, the relative importance of different fouling mechanisms was investigated. The fouling model accounting for membrane morphology was modified to accommodate asymmetric structure. Asymmetric profiles were described by the spatial variation of permeability in the direction normal to the membrane surface. The model predictions were in good agreement with the experimental results based on various composite membranes indicating that composite membranes with a porous structure in upper layer and relative high resistance in lower layer can efficiently
reduce fouling. A-priori estimation of fouling parameters in the combined pore blockage and cake filtration model was proposed to directly relate the fouling parameters with feed characteristics and membrane properties. These works provide important insights into fouling mechanisms during filtration.

A network-based fouling model was developed to simulate the fouling processes. In contrast to the fouling models based on the continuum approaches, network modeling is able to provide more information about the fouling processes within the membrane structure. A network was constructed accounting for asymmetric membrane structure, and the fouling mechanisms within the network were described by particle straining, particle trapping, and particle packing. The permeability of the fouled network was evaluated based on the effective bond size which is correlated with each fouling mechanism. The network modeling was validated by performing filtration experiments with asymmetric membranes having different substrucute. All results indicated that the interplay between the membrane structures and the foulant particles had significant impact on the fouling behavior. It also demonstrated that a graded pore structure could mitigate the fouling by distributing the foulant particles within the entire structure. Despite large-scale computer simulations, the network modeling leads to better understanding of the fouling mechanisms, and provides more degrees of freedom for designing new asymmetric membranes with better fouling resistance.
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1.1 Membrane Technology

1.1.1 Definition of Membrane

Membrane technology is a rapidly emerging field, and has been applied to many areas of separation. There are many membrane processes, based on different separation principles or mechanisms and specific problems can cover the broad size range from particles to molecules [1]. A membrane is a selective barrier between two phases. The phase in the upstream side is usually considered as the feed, while the phase in the downstream side is considered as the permeate.

The performance of a given membrane is mainly determined by two parameters, selectivity and the flow rate through the membrane. The selectivity is determined by the pore size distribution and the surface properties of membrane materials. It can be directly related to the sieving coefficient $S$

$$S = \frac{C_p}{C_f}$$

where $C_p$ and $C_f$ are the solute concentration in the permeate and feed solutions, respectively. The volumetric flow rate per unit membrane area, or flux $J$, is proportional to the driving force in many cases. For the pressure-driven process, the flux-force relationship can be described by a linear phenomenological equation:
The phenomenological coefficient $k$ is called permeability coefficient or Darcy permeability.

1.1.2 Membrane Processes and Membranes for Bioseparation

Membrane technology has been widely used for bioseparations, such as protein separation or purification [2-6], sterile filtration [7-10], bioreactors [11-14], and so on. Although essentially all kinds of membrane processes are applicable to the field of bioseparations, the most interest has been in the application of the pressure-driven membrane processes. Many membranes with different materials and different morphologies have been developed for better performance in bioseparations.

1.1.2.1 Pressure-driven Membrane Processes

Various pressure-driven membrane processes can be applied to bioseparations. These different membrane processes can be distinguished according to solute particle size and membrane structure. These pressure-driven membrane processes were summarized by van Reis and Zydney in their review article on bioprocess membrane technology in 2007 [15].

In Figure 1.1, we can see that microfiltration was designed to remove cells and cell debris while allowing smaller solutes like proteins to pass through the membrane. Ultrafiltration membranes have smaller pore size range than that of microfiltration membranes, and are designed for retaining proteins or other macromolecules.
Specially, virus filtration was sorted as a membrane process between microfiltration and ultrafiltration in van Reis and Zydney’s review [15]. Virus filtration can provide a robust, size-based viral clearance mechanism that complements other virus clearance steps in the production of biotherapeutics [16]. Nanofiltration was designed for separating different solvents with relatively small molecular weight based on both physicochemical and size-based mechanisms [17, 18]. Reverse osmosis is mainly used for the production of high quality water [19].

1.1.2.2 Membrane Materials and Membrane Morphology

There are a number of preparation techniques for constructing various membranes from different materials. The membrane morphology or structure is intrinsically related to the membrane materials and preparation techniques. We can classify the synthetic membranes by their morphology, and two types of membrane may be distinguished: symmetric and asymmetric membranes.

Symmetric membranes have a uniform structure through the depth of the membrane. Roughly, there are two different typical structures of symmetric membranes. Figure 1.2(a) depicts a symmetric membrane with straight-through cylindrical pores. This kind of membrane can be prepared by a track-etch process on a very thin film of polycarbonate or polyester [20-22]. Some ceramic membranes, like aluminum oxide membrane [23, 24], can also have this noninterconnected pore structure. In addition to membranes with circular straight-through pores, there are membranes with slotted pores [25] and elliptical pores [26]. Figure 1.2(b) shows a
highly interconnected porous membrane structure. These porous structures can be made by phase inversion [27, 28], or stretching [29, 30]. Typical materials for preparing the porous membranes are polyvinylidene fluoride (PVDF) [31], polytetrafluoroethylene (PTFE) [32], polyethersulfone (PES) [33], and so on.

A breakthrough in industrial applications was the development of asymmetric membranes [34]. Asymmetric membranes usually consist of a very thin selective skin supported by a porous substrate. The substrate may have a gradient structure, in which pore size gradually increases from the skin to the opposite side as shown in Figure 1.3(a), e.g., Millipore’s Retrovirus membrane (Millipore Corp., Bedford, MA). The transition between the skin and the substrate may be very sharp to form a relatively uniform substrate layer as shown in Figure 1.3(b), e.g., Millipore’s Viresolve 180 membrane (Millipore Corp., Bedford, MA). These asymmetric structures can be made by immersion casting methods [28, 35-37]. In contrast to the single layer structure, composite membranes combine two different structures into a single membrane as shown in Figure 1.3(c). This kind of membrane can be prepared by casting a thin dense layer onto a preformed microporous membrane, which could have symmetric or asymmetric structure [38]. This provides many degrees of freedom to tailor the structure to various types of feed streams [15]. There are a number of polymeric materials for forming the asymmetric membranes, e.g., polyvinylidene fluoride (PVDF) [39], cellulose acetate (CA) [40], polyimide (PI) [41], and so on.
1.2 Membrane Fouling During Microfiltration

1.2.1 Fouling Mechanisms

Membrane fouling is a critical factor in many bioseparation processes, like clarification of protein solutions from harvested cell culture media [42, 43], and plasma collection from whole blood for therapeutic and commercial uses [44]. The irreversible alteration caused by membrane fouling may lead to severe flux decline and alteration of membrane rejection properties [45-48]. Therefore, in the realistic design of a membrane process, the key characteristics are supposed to include the system capacity, which was defined as the volume of feed processed per unit membrane area before the membrane must be regenerated or replaced [15].

Membrane fouling is mainly caused by particle straining based on relative size or particle adsorption based on the interaction between particles and membrane. Here, the particle represents the foulant in feed solution. Either or both of these two fouling mechanisms may be dominant during the membrane filtration, and they have been extensively studied.

1.2.1.1 Particle Sieving

Particle sieving can occur when the particle size is larger than the membrane pore size [49, 50]. During the microfiltration for protein solutions, the membrane fouling is mainly caused by the rejection of large protein aggregates. For example, many previous studies [51-55] found that the flux decline during the filtration of bovine serum albumin (BSA) was associated with the deposition of large protein
aggregates on the membrane surface. Maruyama et al. [56] studied the factors of the protein denaturation and aggregation, such as stirring shear stress and intermolecular exchange of disulfide during the filtration. In addition to the protein aggregates, cell and cell debris can also be the foulant during the filtration [57-59]. All these kinds of foulant particles may be rejected on the membrane surface or strained within the membrane structure. A cake layer may be formed within the blocked region as more particles deposited [60, 61]. Although particle sieving is based on the size exclusion, particle-particle and particle-membrane interactions can affect sieving by increasing or decreasing the rate of particle capture.

1.2.1.2 Particle Adsorption

Adsorptive capture is based on the particle-membrane interactions, including electrostatic interactions and van der Waals forces, or other interaction potentials. When the particle size is much smaller than the membrane pore size, adsorption is supposed to be the dominant mechanism during the fouling. The internal adsorption onto the membrane walls will result in the reduction of membrane permeability [62, 63]. Particle-particle interaction may be involved in this process. For example, some previous studies [64, 65] show that the BSA adsorption involved a rapid adsorption in the early stage of filtration followed by a slow multilayer adsorption that dominates the long term filtration performance. Zydney and Pujar [66-68] studied the effects of longer-range colloidal interactions on the rate of solute transport, and found that the longer-range interactions, e.g., electrostatic force, might improve the
selectivity of membrane system.

1.2.2 Characterization of Membrane Fouling

Characterization of membrane fouling or fouled membranes is critical to understand the fouling mechanisms. Membrane fouling by proteins was traditionally characterized by measuring flux decline [46, 69-71] and rejection change [72-74] during the fouling. Flux decline is easy to measured, and the rate of flux decline will directly affect the system capacity. Flux decline measurement also provides critical information for developing mathematical models, which could provide deep insight into the fouling mechanisms [75, 76].

More and more modern techniques have been applied to the characterization of fouled membranes. In the review article of Chan and Chen [77], the methods for characterizing membrane fouling was classified in terms of their different uses: i) methods for identifying where the fouling is occurring and how much is being deposited, e.g., scanning electron microscopy (SEM) [78, 79], microspectrophotometry [80], and attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) [81, 82]; ii) methods for specifying the proteins in a mixture of two or more species, e.g., confocal microscopy [83-85], and matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) [86-88]; iii) methods for examining the foulant morphology, e.g., atomic force microscopy (AFM) [84, 89-91], and surface force apparatus (SFA) [91-94]. Besides, some modern techniques were used to analyze the particle size distribution in the feed
solutions. For example, Higuchi et al. applied both flow cytometry and light scattering measurements to the analysis of the aggregated size distribution of γ-globulin and albumin in aqueous solution [95].

Recent acoustic studies have reported considerable success in real-time monitoring of membrane fouling on a variety of membrane modules [96-98]. Kujundzic et al. [99] summarized the recent developments in ultrasonic reflectometry that use both time-domain (UTDR) and frequency-domain (UFDR) spectra for noninvasive, real-time assessments of fouling in a variety of module configurations.

1.2.3 Design of Antifouling Membranes

There are a variety of ways to reduce the membrane fouling during the filtration in terms of the different fouling mechanisms. The most extensively studied approach is to modify the membrane materials for minimizing particle-membrane interactions. Besides, more and more studies have revealed that the membrane fouling could be significantly affected by the membrane morphology, and a membrane with some special substructures might have better fouling resistance.

1.2.3.1 Modification of Membrane Materials

Many investigations have shown that increasing membrane surface hydrophilicity could effectively weaken the adsorption of proteins onto the membrane surface [100-105]. Therefore, the most effective method to reduce the protein-membrane interactions is to modify the membrane surface with hydrophilic modifiers.
Hydrophilic monomers can be added onto the membrane surface by chemical-grafting [106], UV-induced grafting [107, 108], plasma-induced grafting [109], and so on. Hydrophilic polymers can be blended with the hydrophobic polymers to fabricate the antifouling membranes. For example, polyethersulfone (PES), which is hydrophobic, can be blended with cellulose acetate phthalate (CAP) [110], or sulfonated polyethersulfone (SPES) [111]. Recently, the method of grafting is combined with the method of blending by using amphiphilic graft copolymers to prepare the antifouling membranes or as additives, e.g., poly(phthalazinone ether sulfone ketone)-graft-poly(ethylene glycol) (PPESK-g-PEG) [112], polyacrylonitrile-graft-polyethylene oxide (PAN-g-PEO) [113, 114], poly(ethylene glycol)-graft-polyacrylonitrile (PEG-g-PAN) [115], and so on. This is an in situ self-organizing modification approach due to the spontaneous migration of hydrophilic polymer onto both membrane surface and inside pores. In addition, interfacial polymerization [116], low temperature plasma treatment [117, 118], adsorption-crosslinking [119], and electrostatic deposition [120], are also effective methods to improve the hydrophilicity of membranes.

1.2.3.2 Optimizing Membrane Morphology

Membrane morphology refers to the structure of membrane, including pore shape, pore size distribution, pore connectivity, pore density, porosity, and so on. For symmetric membranes, all these factors are constant through the depth of the membrane. For asymmetric membranes, some of these factors may be a function of
the depth of the membrane.

The development of new techniques for membrane preparation makes it possible to fabricate the membranes with more complicated substructures. Some studies revealed that membrane fouling could be significantly affected by membrane morphology.

Charcosset and Bernengo [121] applied confocal scanning laser microscopy (CSLM) to the characterization of microfiltration membranes with different morphologies: a closed-cellular morphology (CA membrane), a ‘lacy’-like morphology (PVDF membrane), and a cylindrical pore morphology (PC membrane). The studies [122, 123] on the filtration with membranes which have porous or straight-through pores experimentally showed that the membrane with porous structure had lower fouling rate during the filtration. Ho and Zydney mathematically modeled the membrane structures with different pore connectivity by varying the permeability ratio of the tangential direction to the normal direction [124], and developed a method to measure the membrane pore connectivity [125]. Chandler and Zydney [25] studied the effects of membrane pore geometry on fouling, and found that the membrane with slotted pores had slower flux decline compared to the membrane with circular pores. Riedl et al. [126] found that the morphology of the membrane surface might affect the pattern of the foulant cake layer. Some studies [127-129] also showed that the porosity of the membrane surface might be related to the fouling rate during the initial filtration.

Asymmetric membranes have the advantage of better selectivity and higher
permeability compared to uniform membranes. It is interesting and crucial to study the effects of the asymmetric structures on the fouling during the filtration. Ho and Zydney successfully modeled the composite membrane composed of a very thin skin layer with straight-through pores and a porous support layer [130, 131]. Ulbrict et al. [132] prepared a novel membranes named DuraPES® with a very pronounced anisotropic (‘hour glass’-like) morphology, from which a better performance of fouling resistance resulted. In addition to the effects on flux decline, some studies [133-135] also provided insights into the mechanisms of solute sieving through multilayer membranes.

Recent studies revealed that the orientation of asymmetric membranes might have an impact on the fouling processes. Millipore’s Viresolve 180 membrane (Millipore Corp., Bedford, MA), which has a very thin skin layer and a porous substrate layer, was used for the normal flow filtration (NFF) with the substrate layer exposed to the feed stream [136]. Syedain et al. [137] quantitatively studied the effects of the orientation of the virus filtration membranes on the protein fouling, and found that the membrane capacity with the substrate layer up (Figure 1.4(b)) was significantly greater than that with the skin layer up (Figure 1.4(a)). The better performance with substrate layer up was attributed to the capture of protein aggregates and other large foulants within the substrate layer thereby protecting the virus-retentive skin layer [15].
1.3 Fouling Models for Microfiltration

A Fouling model is a useful tool to mathematically describe the fouling processes, and provide deeper insight into the fouling mechanisms. A variety of fouling models have been developed and applied to the studies on membrane fouling during filtration. Although these fouling models have different mathematical expressions for the fouling processes, most of them mainly deal with the same three critical problems: i) how to describe the structure of the clean membrane; ii) how to determine the fouling rate during the filtration; iii) how to evaluate the fouled membrane during the filtration.

Membrane fouling is essentially one of the processes of particle transport in flow through porous media. In this sense, there are a variety of similar processes, like deep-bed filtration (DBF). As reviewed by Sahimi et al. [138], there are two basic approaches to modeling of these phenomena: the continuum and statistical approaches. Here, we also employed this idea to discuss the modeling of membrane fouling.

1.3.1 Continuum Approaches to Modeling of Membrane Fouling

Continuum approaches rely on the macroscopic continuum conservation equations, and they generally ignore the exact details of the membrane morphology [139]. Ho and Zydney [140] have reviewed these modeling approaches for membrane bioreactors. Here, we demonstrated how these modeling approaches deal with those three problems as mentioned above, and the typical fouling models were
summarized in Table 1.1 based on these three problems.

1.3.1.1 Classical Fouling Models

The classical fouling models are all single fouling mechanism models, namely, modeling the fouling with only one mechanism for a certain period of filtration. All these models assume that the membrane consists of an array of parallel capillaries, and is macroscopically uniform in the transverse direction. Therefore, the Darcy’s Law (Eq. (1.2)) can be integrated to obtain the flux $J$ as a function of the transmembrane pressure $\Delta p$:

$$J = k \frac{\Delta p}{L_m} = \frac{\Delta p}{\mu R_m}$$  \hspace{1cm} (1.3)

$L_m$ is the thickness of the membrane, $R_m$ is the membrane resistance, and $\mu$ is the viscosity of the solution. Here, the effect of osmotic pressure is neglected since it can become important for ultrafiltration membranes or for heavily fouled microfiltration membranes where the retention of smaller colloidal solutes becomes significant [140].

With respect to the fouling rate, it depends on the applied fouling mechanism. The fouling mechanisms applied by the classical fouling models were reviewed by Hermia [141], and they are: i) pore blockage, ii) cake filtration, and iii) pore constriction. The first two are external fouling, which occur on the membrane surface, and the third one refers to the internal fouling, which occurs within the membrane structure.
The pore blockage model [142, 143] assumes that the flux decline during the filtration is attributed to the blockage of the pores on membrane surface as shown in Figure 1.5(a). Therefore, the fouling rate is related to the rate of the change of unblocked membrane area $A_u$:

$$\frac{dA_u}{dt} = -\alpha Q_u C_b$$  \hspace{1cm} (1.4)$$

$C_b$ is the bulk foulant concentration, and $Q_u$ is the volumetric flow rate within the unblocked area. The pore blockage parameter $\alpha$ is defined as the membrane area blocked per unit mass of foulant. If the possibility that part of the foulant particles may be deposited on the blocked region is included, we can get the so-called intermediate pore blockage model [144]:

$$\frac{dA_u}{dt} = -\alpha Q_u C_b \frac{A_u}{A_m}$$  \hspace{1cm} (1.5)$$

where $A_m$ is the total membrane area. Once the pore is blocked, it is assumed that there is no flow passes through that pore any longer as shown in Figure 1.5(a). Therefore, when we evaluate the fouled membrane during the filtration, the instantaneous total flow rate is supposed to be proportional to the fraction of available membrane area:

$$Q = J_o A_u$$  \hspace{1cm} (1.6)$$

Combining Eqs. (1.3) and (1.6) with Eq. (1.4) or Eq. (1.5), we can obtain the analytical solution of instant total flow rate for complete pore blockage and intermediate pore blockage, respectively:
\( \frac{Q}{Q_0} = \exp \left( -\alpha \frac{\Delta p}{\mu R_m} C_{b,t} \right) \) \hspace{1cm} (1.7)

\( \frac{Q}{Q_0} = \left( 1 + \alpha \frac{\Delta p}{\mu R_m} C_{b,t} \right)^{-1} \) \hspace{1cm} (1.8)

The cake filtration model \([142, 145]\) assumes that there is a uniform permeable cake layer formed on the entire membrane surface, and the flux declines as the growth of the cake layer (Figure 1.5(b)). Therefore, the fouling rate is related to the rate of the change of foulant mass per unit membrane area \( m_p \):

\( \frac{dm_p}{dt} = J C_b \) \hspace{1cm} (1.9)

The instantaneous flux of the fouled membrane is supposed to be uniform since the entire membrane surface is covered by the same cake layer. It gives

\[ Q = J A_m = \frac{\Delta p}{\mu (R_m + R_c)} A_m \] \hspace{1cm} (1.10)

\[ R_c = R' m_p \] \hspace{1cm} (1.11)

Therefore, the analytical solution of the instant total flow rate can be obtained by combining Eqs. (1.9), (1.10), and (1.11):

\[ \frac{Q}{Q_0} = \left( 1 + R' \frac{2\Delta p}{\mu R_m} C_{b,t} \right)^{\frac{1}{2}} \] \hspace{1cm} (1.12)

In contrast to pore blockage and cake filtration, the pore constriction model \([145, 146]\) was used to study the internal fouling since it attributes the flux decline to the membrane pore radius decrease as uniform foulant adsorption on the pore walls (Figure 1.5(c)). Therefore, the fouling rate is supposed to be the rate of change of...
membrane pore volume:

\[
\frac{d}{dt} \left( N_0 \pi r_{mf}^2 L_m \right) = -\alpha_v Q C_b
\]  

\(N_0\) is the total number of membrane pores, and \(r_{mf}\) is the radius of fouled membrane pores. The pore constriction rate coefficient \(\alpha_v\) is defined as the volume of deposited foulant on the pore walls per unit mass of foulant filtered through the membrane. As the membrane pores are assumed to shrink uniformly, the total flow rate can be evaluated by:

\[
Q = J A_m = \frac{\Delta \rho}{\mu R_{mf}} A_m
\]  

\[
R_{mf} = 8 \frac{1}{\varepsilon_{ms}} \frac{r_m^2}{r_{mf}^2} L_m
\]

\(R_{mf}\) is the resistance of internally fouled membrane, and is estimated by the Hagen-Poiseuille equation, which is for the laminar flow in a cylindrical tube. \(\varepsilon_{ms}\) is the porosity of membrane surface, and it works for converting the flux based on the total pore area into the flux based on the total membrane area. Therefore, we can get the analytical solution for instantaneous total flow rate as a function of filtration time by combining Eqs. (1.13), (1.14), and (1.15):

\[
\frac{Q}{Q_0} = \left(1 + \alpha_v \frac{Q_0}{\pi r_m^2 L_m} C_b t \right)^{-2}
\]  

The flux decline behavior for all these classical fouling models can be expressed by a common mathematical form [145, 147]:

\[
\frac{Q}{Q_0} = \left(1 + \alpha_v \frac{Q_0}{\pi r_m^2 L_m} C_b t \right)^{-2}
\]
\[ \frac{d^2 t}{dV^2} = k_{nf} \left( \frac{dt}{dV} \right)^{nf} \]  

(1.17)

or

\[ \frac{dJ}{dt} = -k_n J \left( JA_m \right)^{2-nf} \]  

(1.18)

where \( V \) is the total filtered solution volume, and can be related to the filtrate flux:

\[ J = \frac{1}{A_m} \frac{dV}{dt} \]  

(1.19)

The index \( nf \) and the coefficient \( k_{nf} \) are both functions of fouling models: \( nf = 2 \) is for complete pore blockage, \( nf = 1.5 \) is for pore constriction, \( nf = 1 \) is for intermediate blockage, and \( nf = 0 \) is for cake filtration. The required derivatives in Eq. (1.17) can be evaluated in terms of the filtrate flux [145]:

\[ \frac{dt}{dV} = \frac{1}{JA_m} \]  

(1.20)

\[ \frac{d^2 t}{dV^2} = -\frac{1}{J^2 A_m^2} \frac{dJ}{dt} \]  

(1.21)

Based on Eq. (1.17), the log-log plot of \( \frac{d^2 t}{dV^2} \) versus \( \frac{dt}{dV} \) was used to analyze the flux decline data by fitting \( nf \) from the slope [148-151]:

\[ nf = \frac{d \left[ \log \left( \frac{d^2 t}{dV^2} \right) \right]}{d \left[ \log \left( \frac{dt}{dV} \right) \right]} \]  

(1.22)

1.3.1.2 Combined Pore Blockage and Cake Filtration Model

Many experimental studies [145, 148] provided evidence for a transition in
fouling mechanism during the fouling process. However, the classical fouling models could not describe this transition since they are the fouling models based on single fouling mechanism. Ho and Zydney [75] developed a fouling model which combined both pore blockage and cake filtration.

This multi-mechanism fouling model also refers to the membrane structure as an array of parallel capillaries. Therefore, Eq. (1.3) is still suitable for evaluating the membrane flow rate. Like pore blockage model, it also assumes that the membrane surface is covered by foulant particles gradually as shown in Eq. (1.4). The different thing is that the cake layer formed on the blocked area is permeable, and the resistance of the cake layer increases as more foulant particles are deposited as shown in Eq. (1.9). In addition, the cake layer resistance is a function of not only the filtration time \( t \) but also the time \( t_p \), at which that particular region is first covered by foulant particle due to the time-dependent blockage of the membrane surface. This combined fouling mechanism is schematically shown in Figure 1.5(d).

Therefore, the total flow rate is supposed to be the combination of the flow rate within the unblocked area and the flow rate within the blocked area:

\[
Q = Q_u + Q_b
\]  
(1.23)

\[
Q_u = \frac{\Delta p}{\mu R_m} A_u
\]  
(1.24)

\[
Q_b = \int_{A_b} \frac{\Delta p}{\mu \left( R_m + R_{c0} + R_c \right)} dA
\]  
(1.25)

where \( R_{c0} \) is the initial resistance caused by the interaction between membrane and
foulant particle. We can combine Eqs. (1.4), (1.9), (1.23), (1.24), and (1.25) to yield an mathematical expression for the total flow rate:

\[
\frac{Q}{Q_0} = \exp \left( -\alpha \frac{\Delta p}{\mu R_m} C_i t \right) + \int_0^t \frac{\alpha \Delta p C_b}{\mu (R_m + R_{c0} + R_c)} \exp \left( -\alpha \frac{\Delta p}{\mu R_m} C_i t_p \right) dt_p \quad (1.26)
\]

\[
R_c = \left( R_m + R_{c0} \right) \left[ 1 + \frac{2R' \Delta p}{\mu (R_m + R_{c0})} C_b \left( t - t_p \right) - 1 \right] \quad (1.27)
\]

Numerical integral may be involved to evaluate Eq. (1.26) due to the nonuniform character of foulant particle deposition. Ho and Zydney [75] also developed an approximate solution by assuming a uniform resistance of the foulant layer over the fouled surface of the membrane. All these mathematical models have been validated by a variety of experimental studies on membrane fouling [150, 152-155].

1.3.1.3 Fouling Models Accounting For Membrane Morphology

As mentioned in section 1.2.3.2, membrane morphology has significant impact on the fouling processes. However, the fouling models, which refer to the membrane structure as an array of capillaries, could not account for how the membrane morphology affects the fouling.

On the macroscopic scale, the Darcy permeability \( k \) as in Eq. (1.2) was widely used to characterized the properties of porous materials [156, 157]. Some previous studies [158-160] found that the ratio of the permeability in the horizontal direction \( k_h \) to the permeability in the transverse direction \( k_c \) could be used to characterize the anisotropy of the porous materials. Ho and Zydney [124] developed
a fouling model which accounts for the membrane morphology by employing this
permeability ratio $\frac{k_h}{k_z}$. For a membrane with straight-through pores, the membrane
is extremely anisotropic, and $\frac{k_h}{k_z}$ is equal to zero; for membrane with highly
interconnected pores, the membrane is isotropic, and $\frac{k_h}{k_z}$ is around one.

In Ho and Zydney’s model [124], the flow rate is evaluated through a
cylindrical region. The fluid flow within the membrane structure can be balanced by
combining the Darcy’s Law for each direction and the Continuity Equation [161]:

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r k_r \frac{\partial p}{\partial r} \right) + \frac{\partial}{\partial z} \left( k_z \frac{\partial p}{\partial z} \right) = 0 \quad (1.28)$$

When the membrane is fouled by particles on the membrane surface, the radius of the
cylindrical region can be related to the fraction of the blocked area $\theta$ by taking into
account two different cases: i) central blockage for initial fouling (Figure 1.6(a));

$$\theta = \left( \frac{r_{\text{blocked}}}{r_c} \right)^2 \quad (1.29)$$

ii) central void for highly fouled membrane (Figure 1.6(b)).

$$\theta = 1 - \left( \frac{r_{\text{open}}}{r_c} \right)^2 \quad (1.30)$$

The boundary conditions of Eq. (1.28) is related to the fouling process with
two fouling mechanisms: complete pore blockage and cake filtration.

$$\frac{d\theta}{dt} = \alpha \frac{Q}{A_u} \theta C_b \quad (1.31)$$
\[
\frac{dR_c}{dt} = R' \frac{Q_o}{A_p} C_p
\]  
(1.32)

Combining Eqs. (1.28), (1.31), and (1.32) will yield the pressure profile within the membrane structure. The flow rate can be evaluated by integrating the pressure gradient at membrane surface:

\[
Q_o = \int_{A_p} -k_z \frac{\partial p}{\partial z} \bigg|_{z=0} \, dA
\]  
(1.33)

\[
Q_u = \int_{A_p} -k_z \frac{\partial p}{\partial z} \bigg|_{z=0} \, dA
\]  
(1.34)

The total flow rate is the linear combination of the flow rate within the blocked area and the flow rate within the unblocked area.

This fouling model has been successfully used to account for the effects of highly interconnected pore structure of symmetric membranes on the flux decline behavior [124, 131]. Ho and Zydney [130] also developed a fouling model to account for the composite membrane consisting of a very thin skin layer with straight-through pores and a porous bottom layer. Therefore, the total flow rate of the clean membrane can be evaluated by:

\[
Q_0 = \frac{\Delta p}{\mu (R_{skm} + R_{sub})} A_m
\]  
(1.35)

When the foulant particles are deposited on the skin layer surface, the effects of the foulant particles on the pressure profile within the porous substrate is neglected since the lateral flow makes the entire substructure equally accessible to the filtrate. The fouling rate is related to complete pore blockage and cake filtration. The cake layer
is assumed to be uniform for all blocked areas. Therefore, the flux is uniform for both blocked area and unblocked area, and the fouling rate can be expressed as:

\[ \frac{d\theta}{dt} = \alpha J_{ub} \theta C_b \]  
(1.36)

\[ \frac{dR_r}{dt} = R'J_b C_b \]  
(1.37)

The instantaneous total flow rate of the fouled membrane can be evaluated by:

\[ \frac{Q}{Q_0} = \frac{R_{skin}^2 + R_{skin}R_{sub} + R_{skin}R_{\theta} + R_{sub}R_{\theta}}{R_{skin}^2 + R_{skin}R_{sub} + R_{skin}R_{\ell} + R_{sub}R_{\theta}} \]  
(1.38)

### 1.3.2 Statistical Approaches to Modeling of Membrane Fouling

In contrast to continuum approaches, the statistical approaches rely on a more realistic representation of the pore space, e.g., the network models in which the pore space is represented by a network of interconnected pores, and the statistical physics of disordered media, e.g., percolation theory. Many articles [138, 162-164] have reviewed the network modeling and percolation theory. Although these statistical approaches have been applied to many fields, e.g., deep-bed filtration (DBF) [165-168], preparative chromatography [169, 170], papermaking [171, 172], and so on, only a few studies [173-175] on membrane fouling with network modeling have been reported.

The network modeling of particle flow through porous media generally involves a variety of mathematical tools and large-scale computer simulations. Here, we reviewed this approach based on three key problems (Table 1.2): i) how to construct the network for porous media; ii) how to describe the particle flow within...
the porous media; iii) how to evaluate the hydraulic permeability of the network in the presence of particles.

1.3.2.1 Construction of Network for Porous Media

The history of percolation theory as applied to porous media is closely tied to network, and network models and percolation theory are complementary [162]. The basic ideas in percolation can be illustrated by Figure 1.7. The porous media is represented by a square lattice. The line intersections are called “sites”, which are equivalent to pore bodies, and the segments connecting the sites are called “bonds”, which are equivalent to pore throat. The sites are supposed to be in only two possible states: on, i.e., they are open to flow; off, i.e., they are closed to flow or plugged. The open sites are denoted by a large solid dot on the intersection in Figure 1.7. If the probability $P$ of a site being open is very low as shown by Figure 1.7(a), the lattice will have zero conductivity. As $P$ increases, the sites may become joined into one giant cluster spanning the entire array at some probability (Figure 1.7(b)), which is called the critical probability $P_c$, also known as the percolation threshold.

The network model for porous media was first developed by Fatt [176-178]. Most of the early network models are based on the assumption that the pore intersections do not have any volume, and the network consists of only the bonds (pore throats). Chatzis and Dullien [179] pointed out that the majority of the porosity is attributed to the pore bodies, and they started giving pore bodies both size
and volume. Both these two approaches are nowadays being using depending on different applications. No matter what kind of pore bodies are applied, the bonds are always organized in terms of different lattices, like Voronoi lattice [174, 180-182] (Figure 1.8(a)), triangular lattice [183-187] (Figure 1.8(b)), square lattice [185, 188, 189] (Figure 1.8(c)), modified square lattice [167, 184] (Figure 1.8(d)), and single or double hexagonal lattice [184, 185] (Figure 1.8(e) and (f)).

In terms of the percolation theory, the number of bonds connected to a site is called coordination number $Z$. For example, $Z = 3$ stands for a triangular network, $Z = 4$ stands for a square or modified square network, and $Z = 6$ for a single hexagonal network. Chen et al. [190] studied the effect of the coordination number of network on the transport and deposition of particles in porous media, and found that the coordination number may significantly affect filtration rate, effluent concentration, and pressure drop. Although the random network, e.g., Voronoi type, most closely resembles the porous media, Jerauld et al. [181] revealed that, as long as the average coordination number of a disordered network (of the same dimensionality) is the same as that of a regular network, transport processes in the two networks and their effective properties are, for all practical purposes, identical. With century development of computer power, three-dimensional networks have been getting more applications to porous media [191, 192]. The advantage of multidimensional network models is that they can better represent the connected pore structures with more degrees of freedom.

In order to approximate the various geometries of the pores, different types of
tubes (bonds) with geometrically simple and well-defined shapes were developed. The most wildly used tube is the cylindrical tube as shown in Figure 1.9(b). Ioannidis and Chatzis [193] adopted the rectangular tubes (Figure 1.9(a)) in their network modeling taking into account the rectangular cross-section of pores in reservoir rocks. The converging-diverging constricted tubes were introduced to model the void space of granular porous media [194, 195] as shown in Figure 1.9(c). Burganos et al. [196, 197] applied this constricted tubes to the network simulation of deep-bed filtration.

Determining the pore size distribution is important for the network construction. Mochizuki and Zydney [198] showed that the membrane selectivity can be critically affected by the pore size distribution. The pore size distribution can be experimentally measured by mercury porosimetry or photomicrography [199]. In many theoretical studies [146, 198, 200-202], a log-normal probability density function was employed to approximate the realistic pore size distribution. Zydney et al. [203] studied the different functional forms of the log-normal probability density function, and clarified their discrepancies. The classical form of the log-normal probability density function can be given as:

\[
f_r(r_m) = \frac{1}{\sigma r_m \sqrt{2\pi}} \exp \left[ -\frac{(\ln r_m - \ln \bar{r}_m)^2}{2\sigma^2} \right]
\]  

(1.39)

As mentioned by Zydney et al. [203], \( \sigma^2 \) and \( \bar{r}_m \) are not the variance and mean of the probability density function defined by Eq. (1.39). The definition of the mean \( \bar{r}_m \) and variance \( \sigma_m^2 \) of the pore size distribution, and their relationship to \( \sigma^2 \) and
\( \tilde{r}_m \) can be given as:

\[
\bar{r}_m = \int_0^{\infty} r_m f_r(r_m) dr_m = \tilde{r}_m \exp \left( \frac{\sigma^2}{2} \right)
\]

(1.40)

\[
\sigma_m^2 = \int_0^{\infty} (r_m - \bar{r}_m)^2 f_r(r_m) dr_m = \tilde{r}_m \left[ \exp(2\sigma^2) - \exp(\sigma^2) \right]
\]

(1.41)

Combining Eqs. (1.39), (1.40), and (1.41) yields the modified form [200] for the log-normal probability density function:

\[
f_r(r_m) = \frac{1}{r_m \sqrt{2\pi \ln \left( 1 + \frac{\sigma_m^2}{\bar{r}_m^2} \right)}} \exp \left( - \frac{\ln \frac{r_m}{\bar{r}_m} + \frac{1}{2} \ln \left( 1 + \frac{\sigma_m^2}{\bar{r}_m^2} \right)^2}{2 \ln \left( 1 + \frac{\sigma_m^2}{\bar{r}_m^2} \right)} \right)
\]

(1.42)

In addition to the log-normal form of pore size distribution, some studies [183, 184, 204] also employed a Raleigh form of pore size distribution:

\[
f_r(r_m^*) = 2r_m^* \exp \left( -r_m^* \right)
\]

(1.43)

where \( r_m^* \) is a dimensionless pore radius.

The history of determining the rule for the tube (bond) length is interesting. In Fatt’s study [176], it was assumed that the bond length is inversely proportional to its radius. Mualem [205] made an opposite assumption (the bond length is directly proportional to its radius), and mistakenly attributed this assumption to Fatt [176]. Some studies [186, 187] thought that the length of the tube is not a sensitive parameter, and considered the bonds to have a constant length equal to the mean diameter of the pore size distribution. Imdakm and Sahimi [139] estimated the bond length \( L_n \) based on the experimentally measured porosity \( \varepsilon_m \):
\[ L_n = \frac{\varepsilon_m V_m}{\sum \pi r_m^2} \]  

where \( V_m \) is the total volume of the membrane.

### 1.3.2.2 Particle Flow within Porous Media

In contrast to the discussion about fouling mechanisms for continuum approaches (section 1.3.1), for network modeling, we will discuss not only the mechanisms of particle capture but also how the particles flow within the network.

Leichtberg et al. [206] showed that even for a large ratio of particle diameter to bond diameter (as high as 0.95) the deviation of particle velocity from the average fluid velocity is negligible. Therefore, most of studies [173, 175, 186, 187] on the network modeling explicitly or implicitly employed the assumption that the particles move through the bonds with the average velocity of the fluid in that bond. It is critical to determine the exit path for the particle which is at a node (bond intersection). Rege and Fogler [186, 187] made a rule known as flow-biased probability. In terms of this rule, when a particle encounters a node within the network, the exit channel will be selected randomly, but with a bias toward the paths with greater flow rates.

As discussed in section 1.2.1, there are two critical fouling mechanisms: particle sieving and particle adsorption. These two particle capture processes are also employed in the network modeling for particle flow through the porous media. According to the size-exclusion mechanism, when the particle size is larger than the
bond size selected for it to pass through, this particle can be strained by that bond [187]. When the particle size is smaller than the bond size, it is possible that this particle will be trapped on the bond wall. There two questions regarding this process: i) Will this particle come into contact with the bond wall? ii) Will the bond wall be able to hold this particle?

For the first question, it can be solved by two different approaches: probability approach and trajectory analysis. The probability approach is usually adopted by the network modeling with cylindrical bonds. Stein [207] assumed that the probability of a particle reaching at the tube wall is equal to the fraction of flow rate within an annular space near the tube wall (between \( r_b \) and \( r_b - r_P \)):

\[
P_{wall} = 4 \left[ \left( \frac{r_P}{r_b} \right)^2 - \left( \frac{r_P}{r_b} \right)^3 \right] + \left( \frac{r_P}{r_b} \right)^4
\]  

(1.45)

Duclos-Orsello et al. [175] showed that the Stein Equation (Eq. (1.45)) did not improve the data fitting, therefore, they preferred to employ the ratio of particle size to bond size for this probability estimation:

\[
P_{wall} = \frac{r_P}{r_b}
\]  

(1.46)

The particle trajectory analysis involves complicated mathematical tools since the determination of the flow field within the tube and all the forces and torques acting on the particle is required. In order to account for the effect of curvature of the grain surface on the rate of collecting particle in the packed bed, the converging-diverging constricted tube (Figure 1.9(c)) was widely utilized for
modeling the granular porous media [183, 195-197]. Many studies [194, 208-210] have developed a variety of solutions for the flow field within the constricted tube with different numerical methods. The trajectory function $f_{\text{trajectory}}$ was generally given by a differential form:

$$\frac{dr_{pt}}{dz_a} = f_{\text{trajectory}}(r_{pt})$$  \hspace{1cm} (1.47)

where $r_{pt}$ is the position of particle in radial direction, and $z_a$ is the axial position of the tube. $f_{\text{trajectory}}$ can be developed from the total force and torque balance:

$$\sum F_i = 0$$  \hspace{1cm} (1.48)

$$\sum I_i = 0$$  \hspace{1cm} (1.49)

where $F_i$ and $I_i$ are the various forces and the corresponding torques acting on the moving particle, respectively. The detail of the derivation of the trajectory can be found in Imdakm and Sahimi’s work [139]. Some studies [165, 166, 183] also took into account the effect of Brownian motion of the particles with a diameter less than $0.5 \mu m$. It was shown that the Brownian motion behavior can increase the capture probability.

For the second question, the interaction between the particle and the bond wall is involved. Imdakm and Sahimi [139] employed an inequality developed by Vaidyanathan and Tien [211] to determine whether the particle will be trapped or not:

$$F_s \left(2r_p h_b - h_b^2 \right)^{1/2} \geq 10.205 \pi r_p^2 \tau_w (r_p - h_b) + 3.776 \pi r_p^3 \tau_w$$  \hspace{1cm} (1.50)

where $F_s$ is the attractive surface interaction force, $\tau_w$ is the local shear stress at
the wall, and \( h_b \) is the height of protrusion on bond wall. If this inequality (1.50) holds, the trapping of the particle is possible if it follows a trajectory taking it to the bond wall.

Duclos-Orsello et al. [175] adopted a probability approach to determine the particle trapping. The probability of particle trapping is given by an exponential function based on Arrhenius relationship between particle adhesion efficiency to a plate and the energy barrier:

\[
P_{trap} = a \exp \left( -b \frac{\phi_p}{\kappa T} \right)\]  

(1.51)

where \( \kappa \) is the Boltzmann’s constant, \( T \) is the absolute temperature, \( a \) and \( b \) are both the fitted parameters, and \( \phi_p \) is the energy barrier, which can be estimated by the well-known DLVO theory [212].

Rege and Fogler [187] took into account the effect of several forces, like hydrodynamic, gravitational, and physicochemical, on the adhesion by a lumped parameter \( \theta_b \). It was assumed that the particle will be trapped as the particle flow into the region near the bond wall (between \( r_b \) and \( r_b - \theta_b r_p \)). Therefore, the Stein equation (Eq. (1.45)) can be modified as:

\[
P_{wall} = 4 \left[ \left( \frac{\theta_b r_p}{r_b} \right)^2 - \left( \frac{\theta_b r_p}{r_b} \right)^3 \right] + \left( \frac{\theta_b r_p}{r_b} \right)^4\]  

(1.52)

The lumped parameter \( \theta_b \) can be estimated by a relationship of exponential form:

\[
\theta_b = \theta_{b0} \exp \left( -\frac{v}{v'} \right)\]  

(1.53)
where $\theta_{b0}$ is a parameter dependent on ionic condition, $v$ is the fluid velocity in the bond, and $v^*$ is a critical velocity, which can be estimated by balancing the drag force on particle and the attractive force between particle and bond wall [139, 213-215].

1.3.2.3 Permeability of Network during Filtration

In contrast to the continuum approaches, network modeling has the advantage to predict both the particle retention efficiency and flux decline. The particle retention efficiency is closely related to the capture rate as discussed in section 1.3.2.2. Here, we focus on how to predict the flux decline during the filtration, namely, the evaluation of the permeability of the porous media.

The studies on networking modeling for a cylindrical tube generally employed the Hagen-Poiseuille equation to estimate the flow rate within a clean bond:

$$Q_p = \frac{\pi r_b^4}{8 \mu L_b} \Delta p$$

where $Q_p$ is the flow rate of a single bond, $\Delta p$ is the pressure difference exerted on that bond.

When the particles are trapped on the bond walls, the permeability of the network will be decreased, thereby the flux decline occurs. Some studies [165, 183, 187] employed the equation developed by Happel and Brenner [216] to evaluate the pressure drop caused by one particle deposited on the bond wall:
\[ \Delta p = \frac{12 \mu r_p v_0}{r_b^2} \left[ 1 - \left( \frac{r_p}{r_b} \right)^2 \right]^2 K_1 \]  
\[ K_1 = \frac{1 - \frac{2}{3} \left( \frac{r_p}{r_b} \right)^2 - 0.20217 \left( \frac{r_p}{r_b} \right)^5}{1 - 2.1050 \frac{r_p}{r_b} + 2.0865 \left( \frac{r_p}{r_b} \right)^3 - 1.7068 \left( \frac{r_p}{r_b} \right)^5 + 0.72603 \left( \frac{r_p}{r_b} \right)^6} \]  

The total pressure drop through the fouled bond is the linear combination of the pressure drop of clean tube and the pressure drop caused by particle deposition: 
\[ \Delta p_{total} = \Delta p_{tube} + \sum \Delta p_{particle} \]  

Then, the new effective radius \( r_{be} \) after \( n \) particles can be given by [187, 217]: 
\[ \frac{1}{r_{be}^4} = \frac{1}{r_b^4} + 0.75 \sum_{i=0}^{n} \frac{r_p}{L_p} \left[ 1 - \left( \frac{r_p}{r_b} \right)^2 \right]^2 K_1 \]  

With respect to the clogging caused by particle straining, most of studies [139, 186, 187, 213] assumed that the blocked tubes are impermeable, and the bond radius will be set to zero once the straining occurs. In Davies and Jia’s study [173], the effect of cake layer formed on the porous membrane surface was also included in the evaluation of the permeability change. The resistance of the cake layer is generally evaluated by Kozeny-Carman equation [218]: 
\[ R_c = \frac{45(1 - \epsilon_c)^2}{\epsilon_c \frac{1}{r_p^2} \frac{1}{L_c}} \]  

where \( \epsilon_c \) is the porosity of the cake layer, and \( L_c \) is the thickness of the cake layer.
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<tr>
<td>Model for A Composite Membrane</td>
<td>$\frac{d}{dt}\left[r \frac{\partial}{\partial r}\left(r k_z \frac{\partial p}{\partial r}\right) + \frac{\partial}{\partial z}\left(k_z \frac{\partial p}{\partial z}\right)\right] = 0$</td>
<td>$\frac{Q}{Q_o} = \frac{R_{skin}^2 + R_{skin} R_{sub} + R_{skin} R_{th} + R_{sub} R_{th}}{R_{skin}^2 + R_{skin} R_{sub} + R_{skin} R_{c} + R_{sub} R_{c}}$</td>
</tr>
</tbody>
</table>
Table 1.2 Typical Procedures of Network Modeling for Particle Flow through Porous Media

<table>
<thead>
<tr>
<th>Network Construction</th>
<th>Particle Flow</th>
<th>Network Permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic Elements</td>
<td>Particle Velocity</td>
<td>Pressure Drop of Clean Bond</td>
</tr>
<tr>
<td>Network Lattice</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bond</td>
<td>Shape</td>
<td>Straining</td>
</tr>
<tr>
<td></td>
<td>PSD</td>
<td>Particle Capture</td>
</tr>
<tr>
<td></td>
<td>Length</td>
<td>Trapping</td>
</tr>
</tbody>
</table>
Figure 1.1 Comparison of removal characteristics of different pressure-driven membrane processes [15].
Figure 1.2 Typical structures of symmetric membranes: a) straight-through cylindrical pores b) highly interconnected pores.
Figure 1.3 Typical structures of asymmetric membranes: a) graded pore size distribution b) skin-substrate pore size distribution c) composite membrane.
Figure 1.4 Schematic diagrams of virus filtration membrane during NFF with a) skin layer up and b) substrate layer up.
Figure 1.5 Schematic diagrams of fouling mechanisms: a) pore blockage b) cake filtration c) pore constriction d) combined pore blockage and cake filtration.
Figure 1.6 Schematic diagrams of the top surface of a partially fouled membrane: a) central blockage; b) central void.
Figure 1.7 Schematic diagrams of percolation theory a) square lattice with zero conductivity b) square lattice with threshold conductivity.
Figure 1.8 Typical lattices of 2D network for porous media: a) Voronoi b) triangular c) square d) modified square e) single hexagonal f) double hexagonal.
Figure 1.9 Typical tube shapes: a) rectangular tube b) cylindrical tube c) converging-diverging constricted tube.
CHAPTER 2 Objectives and Outline

2.1 Objectives

Most of previous fouling models were developed for homogeneous membranes with an array of cylindrical pores. Although the fouling model developed by Ho and Zydney [124] is able to account for the membrane morphology, their studies were limited to symmetric structures. Internal fouling was ignored by most combined fouling models, and the effects of membrane structures on the internal fouling remained unknown. Therefore, the overall objective of this thesis was to develop fundamental quantitative understanding of the effects of asymmetric membrane structures on fouling behavior, and optimize the asymmetry of the microfiltration membranes for better fouling resistance. More specifically, this study was designed to:

i. Develop a mathematical model accounting for both external fouling and internal fouling, and investigate the relative importance of different fouling mechanisms;

ii. Extend the fouling model accounting for membrane morphology to account for the asymmetric membrane structures;

iii. Propose a-priori estimation for the fouling parameters in the fouling models based on feed characteristics and membrane properties;
iv. Apply the network approach to the simulation of fouling processes with asymmetric membranes, and investigate the effects of membrane structures on the internal fouling;

v. Obtain quantitative data during constant pressure filtration with membranes having various asymmetric structures to validate the model predictions;

vi. Apply these fouling models to examine the possible development of new asymmetric membranes with better fouling resistance.

2.2 Dissertation Outline

The previous work on membrane fouling was reviewed in CHAPTER 1. CHAPTER 3 summarized the materials, apparatus, and experimental methods commonly used in this thesis.

In CHAPTER 4, a three-mechanism fouling model was developed, and this model was applied to the investigation of relative importance of different fouling mechanisms during filtration.

In CHAPTER 5, the effects of asymmetric membrane structures on the external fouling were theoretically analyzed based on the modified fouling model accounting for membrane morphology, and the model predictions were validated by the filtration experiments with composite membranes.

In CHAPTER 6, we mathematically correlated the fouling parameters for the
combined pore blockage and cake layer fouling model to the feed characteristics and the membrane properties, and the model predictions were validated by both single component solutions and binary mixtures.

In CHAPTER 7, a network-based fouling model was developed for homogeneous membranes and compared to the fouling models based on the conventional approaches.

In CHAPTER 8, we extended the network-based fouling model to account for the asymmetric membrane structures, and investigated the effects of asymmetric structures on the foulant particle distribution within the membrane structures.

The major findings of this work were summarized in CHAPTER 9, and recommendations for future work were discussed.
CHAPTER 3 Materials and Experiment Methods

3.1 Introduction

This chapter outlines the apparatus, materials, and experimental methods that are common to most of the studies in this thesis. Additional details that are specific to the individual sections will be provided in each individual chapter.

3.2 Experimental Materials

3.2.1 Protein Solutions

Two proteins were employed by the filtration experiments in this thesis: i) Bovine serum albumin (BSA) (Initial fractionation by heat shock, catalog number A7906, Sigma); ii) α-Casein (From Bovine Milk, catalog number L7891, Sigma). The protein powder was weighed by digital balance (AG204, DeltaRange, Mettler Toledo). Then, the weighed protein powder was dissolved in the desired volume of deionized water, which had been prefiltered through a 0.22 μm hydrophilic polyvinylidene fluoride membrane (catalog number GVWP04700, Millipore) to remove large particulates. All protein solutions were freshly prepared before each experiment and used within 8 hours of preparation.
3.2.2 Polystyrene Microspheres

A series of polystyrene microspheres with different sizes were purchased from Bangs Laboratories Inc. (Fishers, IN). The detailed particle characteristics provided by the manufacturer was listed in Table 3.1. The polystyrene microspheres have uniform particle size as shown in Figure 3.1. The purchased polystyrene microspheres were a highly concentrated aqueous suspension with mass fraction of 10%. In order to minimize the experimental error, we first prepared a concentrated solution, and then dilute it many times to get the desired solution. We usually prepared the concentrated solution with the same volume as the final solution \( V_{\text{feed}} \). If the dilution factor is \( \gamma \), the volume of aqueous microspheres \( V_{\text{PS}} \) can be calculated by:

\[
V_{\text{PS}} = \frac{C_n V_{\text{feed}}}{\gamma C_n \frac{4}{3} \pi r_p^3 \rho_{\text{PS}}}
\]

(3.1)

where \( C_n \) is the number of microspheres per unit volume of aqueous polystyrene microspheres, and \( \rho_{\text{PS}} \) is the density of solid polystyrene polymer. Both of them can be obtained in Table 3.1. The aqueous polystyrene microspheres were dissolved in prefiltered deionized water, and the freshly prepared solutions were used within 12 hours.

3.2.3 Membranes

Membrane filtration data were obtained with a variety of membranes as listed in Table 3.2. All these membranes can be sorted into symmetric (homogeneous)
membrane and asymmetric membrane as discussed in section 1.1.2.2.

The scanning electron micrographs of the surface of symmetric membranes were shown in Figure 3.2. The Anopore anodized aluminum membrane (Figure 3.2(a)) is produced by electrochemical oxidation of aluminum in the presence of phosphoric, oxalic, sulphuric, or some other acids, and anodized at constant current density or a constant voltage [219]. The idealized anodic alumina structure is characterized by regular pores in the center of hexagonal cells. All pores are parallel to each other without intersection. The polycarbonate track-etched membrane (Figure 3.2(b)) is manufactured from high-quality polycarbonate film with a smooth flat surface and very low level of extractable. The irradiation of the polymeric film with energetic heavy ions leads to the creation of linear narrow paths of intense damage, namely tracks, and then, the straight-through pores can be formed by attacking the latent track with a properly chosen chemical agent [20]. Anopore membranes are naturally hydrophilic while PCTE membranes are chemically modified to render them hydrophilic.

The polyvinylidene fluoride (PVDF) membranes are usually manufactured by phase separation techniques. The viscous solution is first cast on a suitable support, and then immersed in a nonsolvent both. The membrane is formed by polymer precipitation. Depending on the rate of polymer precipitation, microporous membranes with various asymmetry can be obtained [31]. A low precipitation rate usually leads to isotropic membranes as shown in Figure 3.2(c). The PVDF membranes are naturally hydrophobic, like GVHP membranes. Most of the PVDF
membranes used in this thesis are hydrophilic as modified using proprietary surface treatments. The nominal pore size of the PVDF membranes ranges from 0.1 to 0.45 $\mu m$.

Two asymmetric membranes were employed in this study: i) PPVG membrane (Figure 3.3(a)); ii) VP membrane (Figure 3.3(b)). The membrane samples of both these two membranes were provided by Millipore. The PPVG membrane has a very thin microporous skin layer on a uniform macroporous spongy substrate layer as shown in Figure 3.3(a1). The nominal pore size of the skin layer is 20 nm, and the substrate layer has a wider pore size distribution around 0.2 $\mu m$. In contrast to the PPVG membrane, the VP membrane has a gradient pore size profile. The pore size is gradually enlarged from the tight side (skin) to the open side (substrate) as shown in Figure 3.3(b1). The PPVG membrane is made from polyvinylidene fluoride, and the VP membrane is made from polyethersulfone. Both of them are chemically modified to render them hydrophilic. The membrane samples were cut into 25 mm disks for the filtration experiments.

### 3.3 Experimental Methods

#### 3.3.1 Filtration Experiments

All dead end filtrations were performed under constant pressure conditions in a 25 mm diameter ultrafiltration cell (Model 8010, Amicon Co., Beverly, MA) connected to an acrylic solution reservoir. The transmembrane pressure was
provided by compressed air. The pressure level can be steadily varied from 0.5 to 20 psi by a regulator (06B 02807, PRG-101-25, Omega) to limit the initial filtrate flow rate within a certain value for various membranes.

The filtrate was collected by a beaker on a digital balance (PBS3002-S, DeltaRange, Mettler Toledo). Both the differential filtrate volume and the accumulated filtrate volume are automatically recorded by measurement software BalanceFM 1.0 (Appendix C.1) with Matlab R2008a (The MathWorks Inc., MA). All experiments were performed at room temperature (20 ± 2°C).

All filtration membranes were compressed using a pressure 1.5 times higher than the filtration pressure for 30 min prior to the flux decline measurements to minimize the effects of membrane compaction. The dead end filtration was performed without stirring, and the stirrer was removed from the filtration cell.

3.3.2 Membrane and Feed Characterization

3.3.2.1 Scanning Electron Microscopy

Scanning electron microscope (SEM, Phillips XL30) was used to characterize the clean and fouled membranes. For the membrane samples fouled by proteins, the protein deposit was fixed by soaking the membrane in a 2 wt.% formaldehyde solution for 30 min, and then, the samples were cleaned with deionized water and dehydrated by rinsing the samples in a series of ethanol aqueous solutions of increasing concentration (10, 50, 80, and 99.5 wt.%). The ethanol-treated membrane was then air-dried at 4°C. The clean membrane samples and the
membrane samples fouled by polystyrene microspheres were directly air-dried at 4°C. In order to observe the cross-section of the membrane and fouling layer, some membrane samples were fractured in liquid nitrogen. All membrane samples were sputtered with a thin layer of gold for SEM analysis. Some fouled membrane samples were sent to Millipore, and the SEM images were provided by Christina Bondy (Millipore, MA).

### 3.3.2.2 Dynamic Light Scattering

The particle size distribution in the feed solution was determined by dynamic light scattering (DLS) with ALV/LSE-5003 CGS-3 multi-angle spectrometer (ALV GmbH, Langen, Germany). This system was equipped with a 15 mW laser diode and a high gain avalanche photodiode detector. The scattering angle was fixed at 90° and wavelength of 633.0 nm. DLS measures the particle diffusion coefficient which can be used to estimate the particle size based on the Stokes-Einstein equation [220].

The particle size distribution was given as relative intensity of particle number \( \hat{n} \) or relative intensity of particle mass \( \hat{m} \) as a function of particle diameter. The intensity of particle number \( \xi_n \) is proportional to the particle number at each particle size. The relative intensity of particle number \( \hat{\xi}_n \) is defined as:

\[
\hat{\xi}_n = \frac{\xi_n}{\xi_{n\text{max}}} \tag{3.2}
\]

The relative intensity of particle number \( \hat{\xi}_n \) can be converted into the relative
intensity of particle mass \( \xi_m \) by:

\[
\xi_m = \frac{\xi_m 4/3}{\pi r_{\text{pi}}^3 \max \left( \xi_m 4/3 \pi r_{\text{pi}}^3 \right)} \quad (3.3)
\]

Here, it is implicitly assumed that the particle density is constant, and the particle is a perfect sphere.

The DLS measurements were calibrated with a binary mixture containing 0.023 \( \mu m \) and 0.25 \( \mu m \) polystyrene microspheres. These two microspheres shared the same mass concentration (0.001 \( g/L \)). The calibration results were given as both particle number weighed distribution (Figure 3.4(a)) and particle mass weighed distribution (Figure 3.4(b)). It shows that the relative number of the 0.25 \( \mu m \) polystyrene microspheres is too small to be demonstrated in Figure 3.4(a) although it has the same mass fraction as the 0.023 \( \mu m \) polystyrene microspheres.

3.3.2.3 Hydraulic Resistance Measurements

The hydraulic resistance \( R \) of both the clean membrane and the fouled membrane was evaluated by measuring the flow rate of prefiltered deionized water \( Q_w \) as a function of the transmembrane pressure drop \( \Delta p \). The experimental equipment is the same as that for filtration experiment as described in section 3.3.1. The transmembrane pressure drop was varied from 1 to 15 psi. By fitting the experimental data of \( Q_w \) versus \( \Delta p \), we can obtain the value of slope \( \frac{A_w}{\mu R} \) to calculate the value of \( R \).
Table 3.1 Polystyrene Microspheres Used In This Thesis

<table>
<thead>
<tr>
<th>Particle Size (µm)</th>
<th>Catalog Code</th>
<th>Solids Content (wt.%)</th>
<th>Buffer</th>
<th>Density of Solid Polymer ρ_{PS} (g/mL)</th>
<th>C_n Number of Microspheres per mL</th>
<th>Surface Area (µm²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.023</td>
<td>PS02N/8192</td>
<td>10</td>
<td>DI Water</td>
<td>1.05</td>
<td>1.502×10^{16}</td>
<td>2.484×10^{14}</td>
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<tr>
<td>0.053</td>
<td>PS02N/6327</td>
<td>10</td>
<td>DI Water</td>
<td>1.05</td>
<td>1.228×10^{15}</td>
<td>1.078×10^{14}</td>
</tr>
<tr>
<td>0.14</td>
<td>PS02N/8351</td>
<td>10</td>
<td>DI Water</td>
<td>1.05</td>
<td>6.353×10^{14}</td>
<td>4.024×10^{13}</td>
</tr>
<tr>
<td>0.25</td>
<td>PS02N/7307</td>
<td>10</td>
<td>DI Water</td>
<td>1.05</td>
<td>1.228×10^{13}</td>
<td>2.323×10^{13}</td>
</tr>
<tr>
<td>0.46</td>
<td>PS02N/5895</td>
<td>10</td>
<td>DI Water</td>
<td>1.05</td>
<td>1.971×10^{12}</td>
<td>1.242×10^{13}</td>
</tr>
<tr>
<td>0.54</td>
<td>PS03N/5977</td>
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<td>DI Water</td>
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<td>1.161×10^{12}</td>
<td>1.058×10^{13}</td>
</tr>
<tr>
<td>1.01</td>
<td>PS04N/5749</td>
<td>10</td>
<td>DI Water</td>
<td>1.05</td>
<td>1.971×10^{12}</td>
<td>5.658×10^{12}</td>
</tr>
</tbody>
</table>

All information was provided by Bangs Laboratories Inc. (Fishers, IN)
<table>
<thead>
<tr>
<th>Membrane Code</th>
<th>Manufacturer</th>
<th>Catalog Number</th>
<th>Material</th>
<th>Pore Size Rating (µm)</th>
<th>Thickness (µm)</th>
<th>Porosity</th>
<th>Wettability</th>
<th>NWP</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCTP</td>
<td>Millipore, MA</td>
<td>VCTP02500</td>
<td>Polycarbonate</td>
<td>0.1</td>
<td>7 - 22</td>
<td>0.05 - 0.20</td>
<td>Hydrophilic</td>
<td>35</td>
</tr>
<tr>
<td>GTTP</td>
<td>Millipore, MA</td>
<td>GTTP02500</td>
<td>Polycarbonate</td>
<td>0.2</td>
<td>7 - 22</td>
<td>0.05 - 0.20</td>
<td>Hydrophilic</td>
<td>354</td>
</tr>
<tr>
<td>Anopore</td>
<td>Whatman, UK</td>
<td>2250</td>
<td>Anodized aluminum</td>
<td>0.2</td>
<td>60</td>
<td>0.60</td>
<td>Hydrophilic</td>
<td>320</td>
</tr>
<tr>
<td>VVLP</td>
<td>Millipore, MA</td>
<td>VVLP02500</td>
<td>Hydrophilic polyvinylidene fluoride</td>
<td>0.1</td>
<td>125</td>
<td>0.70</td>
<td>Hydrophilic</td>
<td>148</td>
</tr>
<tr>
<td>GVWP</td>
<td>Millipore, MA</td>
<td>GVWP02500</td>
<td>Hydrophilic polyvinylidene fluoride</td>
<td>0.22</td>
<td>125</td>
<td>0.70</td>
<td>Hydrophilic</td>
<td>395</td>
</tr>
<tr>
<td>GVHP</td>
<td>Millipore, MA</td>
<td>GVHP02500</td>
<td>Hydrophobic polyvinylidene fluoride</td>
<td>0.22</td>
<td>125</td>
<td>0.75</td>
<td>Hydrophobic</td>
<td>809</td>
</tr>
<tr>
<td>HVLP</td>
<td>Millipore, MA</td>
<td>GVWP02500</td>
<td>Hydrophilic polyvinylidene fluoride</td>
<td>0.45</td>
<td>125</td>
<td>0.70</td>
<td>Hydrophilic</td>
<td>1711</td>
</tr>
<tr>
<td>PPVG</td>
<td>Millipore, MA</td>
<td></td>
<td>Hydrophilic polyvinylidene fluoride (asymmetric)</td>
<td>0.02 (skin)</td>
<td>150</td>
<td></td>
<td>Hydrophilic</td>
<td>63</td>
</tr>
<tr>
<td>VP</td>
<td>Millipore, MA</td>
<td></td>
<td>Modified polyethersulfone (asymmetric)</td>
<td>0.02 (skin)</td>
<td>150</td>
<td></td>
<td>Hydrophilic</td>
<td>53</td>
</tr>
</tbody>
</table>

All information was provided by manufacturer
Figure 3.1 Scanning electron micrographs of polystyrene microspheres: a) 0.053 µm b) 0.25 µm c) 1.01 µm.
Figure 3.2 Scanning electron micrographs of symmetric membranes: a) Anopore anodized aluminum membrane [128] b) Polycarbonate track-etched membrane c) Polyvinylidene fluoride membrane.
Figure 3.3 Scanning electron micrographs of asymmetric membranes: a) PPVG membrane b) VP membrane (provided by Millipore).
Figure 3.4 Calibration of DLS measurement with binary mixture containing 0.023 µm and 0.25 µm polystyrene microspheres: a) particle number-weighed distribution b) particle mass-weighed distribution.
CHAPTER 4  A Three-Mechanism Model to Describe Fouling of Microfiltration Membranes

4.1 Introduction

As discussed in section 1.2, one of the critical problems governing the performance of the microfiltration processes is biofouling caused by specific interactions between the membrane and various proteins during the filtration process. The irreversible alteration caused by protein fouling leads to severe flux decline and alteration of membrane rejection properties.

In order to provide deep insight into the fouling processes, various fouling models have been developed as summarized in section 1.3. Most of the classical fouling models (section 1.3.1.1) are fouling models based on a single fouling mechanism. The pore blockage model and cake filtration model describe the deposition of foulant on the membrane surface, which represent external fouling. In contrast, the pore constriction model accounts for the fouling which occurs within the membrane structures, i.e., internal fouling.

Although all these classical fouling models provided a mechanistic description for the fouling process, significant discrepancies between the flux decline data and model predictions were often observed. Tracey and Davis [145] showed that at the initial time range the curves of total resistance versus filtration time were concave up
suggesting fouling by a pore constriction or pore blockage mechanism, while the curves were concave down at longer filtration range indicating fouling by a cake filtration mechanism. An alternate approach is to use the exponent $n_f$ in the general governing equation (Eq. (1.17)) to differentiate between different mechanisms [141]. Typically these curves do not show a single $n_f$ value for the entire filtration, but rather one that changes with time.

The combined fouling model developed by Ho and Zydney [75] described the flux decline during fouling by using both pore blockage and cake filtration (section 1.3.1.2). This model showed a smooth transition from pore blockage to cake filtration. Although the combined pore blockage and cake filtration model described the flux decline during BSA filtration through straight-through pore membranes, internal fouling was completely neglected in this combined fouling model. Internal fouling caused by protein adsorption may be important for cases in which the feed stream has a relatively low concentration of foulant. For example, Taniguchi et al. [221] reported some irreversible internal fouling by low molecular weight species.

Many experimental studies revealed that both external fouling and internal fouling could be dominant during the fouling processes. Jegatheesan et al. [222] found that the combination of external and progressive internal fouling models more accurately predicted the performance of treating limed and partially clarified sugar cane juice with ceramic microfiltration membranes. Kumar and Roy [223] showed that an initial intense flux decline due to external blockage followed by an internal deposition or the formation of a cake layer during the filtration of saccharomyces
cerevisiae cells through alumina membranes. Blanpain-Avet et al. [72] investigated the membrane fouling in the sterile microfiltration of beer with an organic membrane, and found that the flux decay was governed by internal fouling at the initial stages, followed by an external surface fouling.

Some studies also showed that both the feed characteristics and membrane properties could affect the dominant fouling mechanisms during the filtration. Guell and Davis [69] filtered a series of protein solutions using polysulfone and polycarbonate membranes, and found that BSA and lysozyme (LY) displayed only internal fouling, whereas ovalbumin (OV) exhibited an initial phase in which internal fouling dominated, followed by external fouling. Mueller et al. [224] tested a series of membranes with different pore size with oily water. The experimental results showed that the 0.2 \( \mu m \) and the 0.8 \( \mu m \) ceramic membranes appeared to exhibit internal fouling followed by external fouling, whereas external fouling characterized the behavior of the 0.1 \( \mu m \) polymer membrane from the beginning of the filtration. Mueller and Davis [129] studied the effects of varying membrane morphology on protein fouling. They found that 0.2 \( \mu m \) PCTE membranes were internally fouled at the initial filtration with external fouling becoming dominant at later times; 0.2 \( \mu m \) CA membranes showed only internal fouling, while 0.2 \( \mu m \) PS and PVDF membranes led to almost immediate external fouling.

All these experimental studies indicate that the combined fouling models are very important for describing not only external fouling but also internal fouling. Bolton et al. [225] used a new method to combine the four classical fouling models.
In this method, five binary combinations of the classical fouling models were developed: cake-complete blocking, cake-intermediate blocking, complete-standard blocking, intermediate-standard blocking, and cake-standard blocking. Some combinations provided good fits for different fouling processes. However, the application of these fouling model combinations needed experimental observation of fouling mechanisms prior to the data fitting.

The objective of this work was to develop a new fouling model accounting for both external fouling and internal fouling, and investigate the relative importance of the different fouling mechanisms with this combined fouling model. In this work, the model assumed the mechanisms were sequential in nature: internal fouling followed by external fouling. The model predictions were validated by comparing the model calculations with experimental flux decline data of four feed-membrane combinations: i) 0.25 µm polystyrene microspheres through 0.2 µm PCTE membranes (external fouling is dominant); ii) BSA solutions through 0.22 µm hydrophobic PVDF membranes (both external and internal fouling are dominant); iii) prefiltered BSA solutions through 0.22 µm hydrophobic PVDF membranes (pore blockage will be reduced); iv) BSA solutions through 0.22 µm hydrophilic PVDF membranes (external fouling will dominate). In this way, the results of this new model were expected to indicate the single mechanism model as the experiment was designed to make that mechanism dominate. Then, through the scaling approach, we theoretically analyzed the relative importance of the different fouling mechanisms based on the three-mechanism fouling model.
4.2 Model Development

We first assumed that the membrane had straight-through cylindrical pores, and the fluid flow can be described by the Hagen-Poiseuille law. The flux decline during the filtration was attributed to three classical fouling mechanisms: pore blockage, pore constriction, and cake filtration. Initially, pore constriction occurred through all the open pores while the membrane surface was blocked gradually by foulant particles to form an inhomogeneous blocked area. We also assumed that once a pore was blocked by an foulant particle deposited on the membrane surface, no further pore constriction can occur. Subsequently, a cake layer was formed within the blocked area. The hydraulic resistance of the cake layer was not uniform, and was dependent on the time when the pores were first blocked by the particles. The regions which were blocked first had the greatest resistance and thus the smallest flux, leading to the slowest rate of cake growth. As a result, the net cake growth was a self-leveling process, with those regions having greater resistance (i.e., thickness) fouling more slowly. The effects of temperature and cross flow on the fouling processes were ignored in the current work. Figure 4.1 schematically shows the combined fouling mechanisms.

In Figure 4.1, it is showed that there are two different regions on the membrane surface: blocked and unblocked regions. Therefore, the volumetric flow rate through the fouled membrane is the summation of the flow rate through the
unblocked regions \( Q_u \) and blocked regions \( Q_b \):

\[
Q = Q_u + Q_b \tag{4.1}
\]

The rate of the change of unblocked membrane area can be described by:

\[
\frac{dA_u}{dt} = -\alpha J_u A_u C_b \tag{4.2}
\]

The pore constriction occurs uniformly within the unblocked pores. Therefore, the filtration flux within the unblocked regions \( J_u \) can be calculated in terms of the classical pore constriction fouling model:

\[
J_u = J_0 \frac{1}{(1 + \beta Q_0 C_b t)^2} \tag{4.3}
\]

\( \beta \) is a lumped fouling parameter indicating the number of membrane pores which could be filled by unit foulant mass convected into the pores:

\[
\beta = \frac{\alpha_v}{\pi r_m^2 \delta_m} \tag{4.4}
\]

Combining Eqs. (4.2) and (4.3), we can first obtain the area of unblocked regions as a function of filtration time:

\[
\frac{A_u}{A_m} = \exp \left( -\frac{\alpha C_b J_0 t}{1 + \beta Q_0 C_b t} \right) \tag{4.5}
\]

Then, the flow rate within the unblocked regions can be evaluated by combining Eqs. (4.3) and (4.5):

\[
\frac{Q_u}{Q_0} = \frac{1}{(1 + \beta Q_0 C_b t)^2} \exp \left( -\frac{\alpha C_b J_0 t}{1 + \beta Q_0 C_b t} \right) \tag{4.6}
\]

Comparing Eq. (4.6) with the classical pore blockage model as showed in Table 1.1,
we can see that the rate of flux decline is slowed down by the pore constriction due to
the reduced convective flow through the constricted pores.

Within the blocked regions, due to the spatial inhomogeneity of the cake layer
and the constricted pores, the volumetric flow rate through the blocked pores is
evaluated as the integral of the flux within the blocked regions over the entire blocked
area:

$$Q_b = \int_{A_b} J_b dA$$ (4.7)

$$J_b = \frac{\Delta p}{\mu (R_{mf} + R_c + R_{c0})}$$ (4.8)

where $R_{mf}$ is the resistance of the internally fouled membrane, $R_c$ is the resistance
of the cake layer over a particular region of the membrane, and $R_{c0}$ is the initial
resistance of single foulant particle deposited on the membrane surface. The foulant
particle layer deposited over a particular region of the membrane only grows over the
time interval $t_p$ to $t$. $t_p$ is the time when the particular region is first blocked.

Once the membrane pores are blocked at time $t_p$, the pore constriction stops with:

$$R_{mf} = R_m \left(1 + \beta Q_b C_b t_p\right)^2$$ (4.9)

As described by the classical cake filtration model, the rate of the change of foulant
cake layer can be determined by:

$$\frac{dR_c}{dt} = f' R' J_b C_b$$ (4.10)

Substituting Eqs. (4.8), (4.9) into (4.10) and solving the obtained differential equation,
we can get the total hydraulic resistance over a particular region within the blocked
regions as a function of filtration time:

\[ R_m + R_c + R_{e0} = \sqrt{R_{e0} + R_m \left(1 + \beta Q_0 C_b t_p \right)^2} + 2 R_m f \mathcal{K} J_0 C_b \left( t - t_p \right) \] (4.11)

The blocked area of the membrane surface increases with filtration time:

\[ dA_b = -dA_u = \frac{\alpha C_b J_0}{(1 + \beta Q_0 C_b t_p)^2} \exp \left( -\frac{\alpha C_b J_0 t_p}{1 + \beta Q_0 C_b t_p} \right) dt_p \] (4.12)

Substituting Eqs. (4.11) and (4.12) into Eq. (4.7) yields the volumetric flow rate through the blocked area:

\[ \frac{Q_b}{Q_0} = \frac{\alpha C_b J_0}{(1 + \beta Q_0 C_b t_p)^2} \exp \left( -\frac{\alpha C_b J_0 t_p}{1 + \beta Q_0 C_b t_p} \right) \int_0^t \frac{1}{\sqrt{R_{e0} + (1 + \beta Q_0 C_b t_p)^2}} + 2 f \mathcal{K} J_0 C_b \left( t - t_p \right) dt_p \] (4.13)

Therefore, we can combine the flow rate within the unblocked area Eq. (4.6) and the flow rate within the blocked area Eq. (4.13) to obtain the total flow rate as a function of filtration time:

\[ \frac{Q}{Q_0} = \frac{1}{(1 + \beta Q_0 C_b t)^2} \exp \left( -\frac{\alpha C_b J_0 t}{1 + \beta Q_0 C_b t} \right) \right. \] \[ + \left. \int_0^t \frac{\alpha C_b J_0}{(1 + \beta Q_0 C_b t_p)^2} \exp \left( -\frac{\alpha C_b J_0 t_p}{1 + \beta Q_0 C_b t_p} \right) \] \[ \frac{1}{\sqrt{\frac{R_{e0}}{R_m} + (1 + \beta Q_0 C_b t_p)^2}} + 2 f \mathcal{K} J_0 C_b \left( t - t_p \right) dt_p \] (4.14)

In this combined fouling model, \( \alpha, \beta, \) and \( f \mathcal{K} \) represent the parameters for pore blockage, pore constriction, and cake filtration, respectively. All of them have physical meaning.
4.3 Experimental Methods

4.3.1 Materials

In order to verify the model predictions with cases in which different fouling mechanisms are dominant, we employed four feed-membrane combinations as listed in Table 4.1. The detailed information about feed characteristics, membrane properties, and solution preparation were introduced in section 3.2. The prefiltered BSA solutions were prepared by filtering BSA solution through a 0.1 µm hydrophilic PVDF membrane (VVLP) prior to the filtration experiments. The concentration of the BSA solutions before and after prefiltration were quantified using a UV-Vis spectrophotometer (Cary50, Agilent) at wave length of 280 nm.

4.3.2 Filtration Experiments

The common performance of filtration experiment was introduced in section 3.3.1. The transmembrane pressure $\Delta p$ applied in this work was 2 psi (14 KPa) for all feed-membrane combinations.

The concentration of polystyrene microsphere solutions was varied from 0.005 to 0.04 g/L, and the concentration of both BSA and prefiltered BSA solutions was varied from 1 to 8 g/L. The concentration of BSA solutions is higher than that of the polystyrene microsphere solutions in that the protein fouling during microfiltration occurs primarily by the deposition of large protein aggregates.
for which the mass fraction is much lower than that of protein monomer. The hydrophobic PVDF membranes (GVHP) were wetted by pure ethanol prior to the filtration experiments.

4.4 Results and Discussion

4.4.1 Model Validation and Parameter Estimation

As a first step to validate the three-mechanism model, carefully chosen cases were tested to verify that the model and fitting procedure were functioning properly. These cases corresponded to extreme cases, where one particular mechanism was expected to dominate the fouling. The flux decline data were also replotted as total resistance versus filtration time to examine the underlying fouling mechanism. Tracey and Davis [145] showed that the $R_{\text{t}}$ curve is concave up when $nf > 1$ (pore constriction and pore blockage), and is concave down when $nf \leq 1$ (intermediate pore blockage and cake filtration).

4.4.1.1 Polystyrene Microspheres through PCTE Membrane

In the first system, 0.25 $\mu$m polystyrene microspheres were filtered through 0.2 $\mu$m PCTE membranes. As mentioned in section 3.2.3, track-etched membranes have uniform straight-through cylindrical pores. As the microsphere size is larger than the membrane pore size, the polystyrene microspheres are expected to be completely rejected on the membrane surface. Therefore, pore blockage and cake
filtration will be the dominant fouling mechanisms for this case.

The filtration experimental results were plotted as normalized flow rate versus filtration time as shown in Figure 4.2(a). The initial flow rate for various concentrations ranged from $1.2 \times 10^{-7}$ to $1.4 \times 10^{-7}$ m$^3$/s. As the concentration of the polystyrene microspheres increased, the rate of flux decline increased. During the initial filtration, sharp decay of normalized flow rate was observed for all concentration levels. The rate of flux decline was significantly reduced after about 1 h filtration.

In Figure 4.2(b), the total hydraulic resistance of the fouled membrane was calculated based on the flow rate data in Figure 4.2(a) ($R_{total} = \frac{\Delta P A_m}{\mu Q}$), and plotted as a function of filtration time. This plot shows that the $R_{total}$ versus filtration time curves are clearly concave down over almost the full time range except for the narrow initial period, suggesting a cake filtration mechanism for the entire filtration. We calculated the filtration time required to achieve monolayer coverage based on the membrane area and particle size by assuming all microspheres convect to the membrane surface. This corresponds to only $5.4 \times 10^{-5}$ g which can occur within 3 min for the lowest concentration level (0.005 g/L). The short time period for achieving complete surface coverage explains why the pore blockage region (concave up) was not observed in Figure 4.2(b).

4.4.1.2 BSA through Hydrophobic PVDF Membrane

As discussed in section 1.2.3.1, the hydrophobic membrane surface could
increase the adsorptions of protein onto the membrane pore wall. Therefore, in the second system, we filtered standard BSA solutions through 0.22 µm hydrophobic PVDF membranes (GVHP) with the concentration varying from 1 to 8 g/L as shown in Figure 4.3(a). The initial flow rate for various concentrations ranged from 1.3×10^{-7} to 1.4×10^{-7} m^3/s. In contrast to the results of polystyrene microspheres, it yielded slower flux decay during the entire filtration for BSA through the hydrophobic PVDF membrane.

The data shown in Figure 4.3(a) were replotted in Figure 4.3(b) as total resistance versus filtration time. The total resistance versus filtration time curves at low concentrations (1 and 2 g/L) seem quite linear. This is likely due to the fact that fouling occurred through a combination of different fouling mechanisms. In these cases, the total resistance versus filtration time curves alone did not provide a clear indication of the dominant fouling mechanism. The different fouling mechanisms can be distinguished using our three-mechanism model which will be discussed in more detail later. At a higher concentration, the data showed a transition from concave up during the initial time to concave down at long filtration time. This indicates that the fouling was mainly caused by pore blockage and pore constriction during the early stage of filtration, and dominated by cake filtration at longer filtration time.

4.4.1.3 Prefiltered BSA through Hydrophobic PVDF Membrane

In order to reduce the extent of fouling by pore blockage and cake filtration
with protein aggregates and allow pore constriction to be dominant, BSA solutions were first prefiltered through a 0.1\( \mu m \) hydrophilic PVDF membrane prior to the filtration through 0.22\( \mu m \) hydrophobic PVDF membrane. The UV spectrophotometer measurement shows the concentrations of the BSA solutions were all within 97\% of the BSA concentration before prefiltration. This indicates that the prefiltration with a 0.1\( \mu m \) hydrophilic PVDF membrane did not reduce the concentration of BSA monomers significantly.

Figure 4.4(a) shows the experimental results of the filtration of prefiltered BSA through a 0.22\( \mu m \) hydrophobic PVDF membrane. The filtration time was extended to 300 min for achieving steady state. The overall flux decline behavior is similar to the standard BSA solutions (Figure 4.3(a)). We also note that, at high concentration level (8 g/L), the flux decline curve for standard BSA solution reached steady state within 120 min while it took almost 300 min for the prefiltered BSA solution to get the same tendency.

In the plot of total resistance versus filtration time (Figure 4.4(b)), the curves for lower concentrations (1 and 2 g/L) seems linear. At a higher concentration, the total resistance versus filtration time curve is concave up during the entire filtration indicating fouling by the pore blockage or pore constriction. We will identify the fouling mechanism with the best fit fouling parameters based on the three-mechanism fouling model later.
4.4.1.4 BSA through Hydrophilic PVDF Membrane

In the fourth system, the 0.22 $\mu m$ hydrophilic PVDF membrane was employed to filter the standard BSA solution. The experimental data were shown in Figure 4.5(a) and (b) for flux decline versus filtration time and total resistance versus filtration time, respectively. The initial flow rate through the hydrophilic PVDF membranes was slightly lower than the hydrophobic PVDF membranes ranging from $1.0 \times 10^{-7}$ to $1.1 \times 10^{-7} \text{ m}^3/\text{s}$ for various BSA concentrations.

Compared to the filtration through hydrophobic PVDF membranes as shown in Figure 4.3(a), the rate of flux decline through hydrophilic PVDF membranes was lower. This is consistent with the earlier studies indicating that the hydrophilic membranes reduce protein adsorption within the membrane structures (section 1.2.3.1). The total resistance versus filtration time curves are concave down indicating that the fouling is mainly caused by the cake filtration mechanism.

4.4.2 Fouling Parameter Estimation and Analysis

The best fit parameters were obtained by minimizing the sum of squared residuals between the model calculations and the experimental results. The solid curves in Figure 4.2 to Figure 4.5 represent the model calculations based on the best fit parameters listed in Table 4.2. The modeling results are in good agreement with the experimental data for all tested feed-membrane combinations.
4.4.2.1 Parameter for Pore Blockage

Fouling parameter $\alpha$ is defined as the blocked membrane area per unit foulant mass convected to the membrane surface denoting the rate of pore blockage. The value of $\alpha$ for polystyrene microsphere solutions through PCTE membrane is much larger than that for BSA solutions. This is because almost all polystyrene microspheres in the solution contribute to the pore blockage, while only the small fraction of BSA present as aggregates are large enough to block the membrane pores. The value of $\alpha$ for prefiltered BSA solutions is much smaller than that for standard BSA solutions. This indicates that most of the protein aggregates present in the BSA solutions have been removed by 0.1 $\mu$m hydrophilic PVDF membrane.

4.4.2.2 Parameter for Pore Constriction

The pore constriction parameter $\beta$ indicates the number of membrane pores filled by unit foulant mass convected into the membrane structure. Therefore, the value of $\beta$ for polystyrene microspheres through the PCTE membrane was equal to zero. This is consistent with the expectation that polystyrene microspheres can not enter the membrane structure with a pore size smaller than the size of the microspheres. The values of $\beta$ for standard and prefiltered BSA solutions through the hydrophobic PVDF membranes are quite similar indicating that the prefiltration step eliminates only large protein aggregates but not protein monomers or oligomers. It is interesting to note that the value of $\beta$ for BSA solutions through hydrophilic membranes is significantly smaller than that for BSA solutions filtered through
hydrophobic membranes. This is very consistent with the expectation that hydrophilic membranes can minimize the protein adsorption within the membrane structures.

4.4.2.3 Parameter for Cake Filtration

The specific cake layer resistance \( fR' \) is the proportional coefficient for the differential rate of the growth of the cake layer resistance. \( fR' \) for prefiltered BSA solutions is smaller compared to BSA solutions. This is due to the fact that the fouling layer is formed mainly by protein aggregates in the case of standard BSA solutions, while it was formed by protein monomers or oligomers in the case of prefiltered BSA solutions. This also explains the larger value of the initial resistance of single foulant particle \( R_{c0} \) for standard BSA solutions.

Although the fouling parameters were obtained from fitting the experimental data, the values of the parameters are consistent with the expectation based on the experimental systems being designed to emphasize different fouling mechanisms. This suggests that our model combining all three fouling mechanisms gives a good description for flux decline caused by different mechanisms and the best fit parameters provide a good indication of the system characteristics.

4.4.3 Flux Decline Analysis with \( \frac{d^2t}{dV^2} - \frac{dt}{dV} \) Plot

In order to distinguish different fouling mechanisms during the filtration processes, we also employed the log-log plot of \( \frac{d^2t}{dV^2} \) versus \( \frac{dt}{dV} \) to analysis the
flux decline data. The required derivatives can be evaluated in terms of the filtrate flux with Eqs. (1.20) and (1.21). The values of $\frac{dJ}{dt}$ in model calculations were evaluated numerically by differentiating the flux versus filtration time data with five points forward difference derivative formula [226]. For experimental data, the values of $\frac{dJ}{dt}$ were obtained by numerical difference based on three-point stencil. The value of $nf$ can be obtained by fitting the slope of the $\frac{d^2t}{dV^2}$ versus $\frac{dt}{dV}$ curves as shown in Eq. (1.22).

4.4.3.1 Polystyrene Microspheres through PCTE Membrane

For the case of polystyrene microsphere solutions through PCTE membranes (Figure 4.6), both the experimental data yield a negative slope followed by a zero slope on the log-log plot. This behavior was very accurately described by the model calculations, even though these results can not be explained by any of the classical fouling models, all of which yield positive initial slopes. The initial decrease in $\frac{d^2t}{dV^2}$ indicates a reduction in the rate of flux decline $\frac{dJ}{dt}$ due to the relatively small resistance provided by polystyrene microsphere cake layer. During the initial filtration, $\frac{dJ}{dt}$ decreases much more rapidly than $J$. In contrast, at longer filtration time, both of them are balanced by each other to yield a constant $\frac{d^2t}{dV^2}$ indicating the fouling by cake filtration mechanism ($nf = 0$). Note that the data obtained at higher concentration start at higher value of $\frac{dt}{dV}$. This is due to the rapid flux decline for higher concentration which gives a lower initial flux.
4.4.3.2 BSA through Hydrophobic PVDF Membrane

Figure 4.7 shows the log-log plot of $\frac{d^2t}{dV^2}$ versus $\frac{dt}{dV}$ based on the experimental data in Figure 4.3(a). The solid curves are model calculations using the best fit fouling parameters listed in Table 4.2. The experimental data yield a quite linear relationship with slope 1.46 on the log-log plot. The slope of 1.5 indicates that the fouling was dominated by pore constriction. However, as we can see in section 4.4.2, the fouling parameter analysis verifies the multiple fouling mechanisms for BSA solutions filtering through the hydrophobic membranes. The modeling also predicts a constant value of $\frac{d^2t}{dV^2}$ at very long filtration time ($\frac{dt}{dV} > 1.4 \times 10^8 \text{s/m}^3$ or $\frac{Q}{Q_0} < 0.1$). This behavior corresponds to the cake filtration. The asymptotic value of $\frac{d^2t}{dV^2}$ increases linearly with protein concentration due to the increase in rate of cake growth shown by Eq. (4.10).

4.4.3.3 Prefiltered BSA through Hydrophobic PVDF Membrane

When the BSA solutions were prefiltered to remove the protein aggregates prior to the filtration with hydrophobic membranes, the log-log plot of $\frac{d^2t}{dV^2}$ versus $\frac{dt}{dV}$ exhibits linear relationships with a slope of 1.5 (Figure 4.8). This value is consistent with the fouling dominated by pore constriction. The modeling did not show a constant $\frac{d^2t}{dV^2}$ region representing the cake filtration. This is because the
filtration time required for achieving the region when the cake filtration begins to dominate (slope is lower than 0.01) is 1600 h for the concentration level 1 g/L. However, for the standard BSA solution, only 50 h is required to achieve the same region of cake filtration for the same concentration level.

4.4.3.4 BSA through Hydrophilic PVDF Membrane

The log-log plot of \( \frac{d^2t}{dV^2} \) versus \( \frac{dt}{dV} \) for the system of standard BSA solutions filtered through the hydrophilic membranes was shown in Figure 4.9. The initial slope ranges from 1.92 to 1.95. These values are very close to 2 indicating the complete pore blockage mechanism. The curves reach a maximum before the decay as observed in previous studies [75, 145]. As shown by the model predictions, all curves achieve the constant \( \frac{d^2t}{dV^2} \) region after the decay.

4.4.4 Relative Importance of Different Fouling Mechanisms

It is important to study the effects of the relative importance of different fouling mechanisms on the fouling processes as more than one fouling mechanism could be dominant in many realistic filtrations. In order to more efficiently analyze the relationships between different fouling mechanisms, we employed the scaling approach [227, 228] to simplify the complicated model equation (Eq. (4.14)). Scaling analysis of a system provides more insights into the desired target in a simple way, and helps us to obtain a better knowledge of the studied system.

Following the steps of scaling approach developed by Krantz [227], we can
obtain the dimensionless form of the combined fouling model:

\[
\frac{Q}{Q_0} = \frac{1}{\left(1 + \frac{t_s}{t_{\beta}}\right)^2} \exp\left(-\frac{t_s}{t_{\alpha}} + \frac{t_s}{t_{\beta}}\right)
\]

\[
= \frac{t_s}{t_{\alpha}} \frac{1}{\left(1 + \frac{t_s}{t_{\beta}}\right)^2} \exp\left(-\frac{t_s}{t_{\alpha}} + \frac{t_s}{t_{\beta}}\right)
\]

\[
+ \int_0^{t^*} \frac{1}{\sqrt{\frac{R_{c0}}{R_m} + \left(1 + \frac{t_s}{t_{\beta}}\right)^2 t_p^*}} + 2 \frac{t_s}{t_{\beta}} \left(t^* - t_p^*\right) dt_p^*
\]

where \( t_s \) is the scaling factor for filtration time. In bounding the dimensionless time group to be \( o(1) \), we have four possible time scales. The first one is the observation time \( t_o \). Obviously, \( 0 \leq t_o < \infty \) since this time scale is the actual filtration time in terms of the experimental process. The other three time scales \((t_\alpha, t_\beta, \text{ and } t_\gamma)\) are related to the rate of different fouling mechanisms as defined in Table 4.3.

\( t_\alpha \) is the characteristic time for pore blockage. It denotes the time required to yield complete coverage of the membrane surface at the constant filtrate flux \( J_o \). The reciprocal of \( t_\alpha \) is equal to the normalized initial rate of pore blockage. Therefore, the value of \( t_\alpha \) is inversely proportional to the rate of pore blockage. We calculated the value of \( t_\alpha \) for different feed-membrane combinations based on the best fit fouling parameters shown in Table 4.2. In Table 4.4, it shows that the system of polystyrene microspheres through PCTE membrane has the smallest \( t_\alpha \) indicating the highest rate of pore blockage. The value of \( t_\alpha \) for prefiltered BSA
solution is much larger than those for standard BSA solutions through both hydrophobic and hydrophilic membranes. This is consistent with the fact that the large protein aggregates have been removed by the prefiltration.

\( t_\beta \) is defined based on the fouling parameter \( \beta \) for pore constriction. It represents the time required to fully fill one membrane pore at constant flow rate \( Q_0 \). The reciprocal of \( t_\beta \) is the normalized initial rate of the change of pore volume. In Table 4.4, we can see that \( t_\beta \) for polystyrene microspheres through PCTE membrane is infinitely large since all particles are rejected on the membrane surface. BSA and prefiltered BSA solutions through hydrophobic PVDF have the similar \( t_\beta \) for which value is significantly smaller than that for BSA solution through hydrophilic PVDF. This again verifies that the hydrophilic membranes can minimize the adsorption of proteins onto the membrane pores.

The time scale for cake filtration is \( t_\gamma \) representing the time required to form a cake layer of which hydraulic resistance is equal to the membrane resistance at constant filtrate flux \( J_0 \). It is inversely proportional to the rate of the cake layer resistance change. As shown in Table 4.4, the value of \( t_\gamma \) for the prefiltered BSA solution is much larger than that for the other cases in that the growth of cake layer on membrane surface is mainly attributed to the large aggregates in BSA solutions.

In order to analyze the relative importance of different fouling mechanisms, the characteristic time of pore blockage \( t_\alpha \) is chosen as the time scale. Therefore, the dimensionless combined fouling model is dependent on three dimensionless
groups: \( \frac{R_{c0}}{R_m} \), \( \frac{t_t}{t_r} \), and \( \frac{t_t}{t_{\beta}} \). These dimensionless groups indicate the rate ratio of different fouling mechanisms. In the following sections, we will employ the log-log plot of \( \frac{d^2t}{dV^2} \) versus \( \frac{dt}{dV} \) again to study how these dimensionless groups affect the fouling processes.

4.4.4.1 Effects of Initial Resistance of Single Fouulant

\( \frac{R_{c0}}{R_m} \) is the resistance ratio of single foulant particle to the membrane. The effects of \( \frac{R_{c0}}{R_m} \) on the fouling process was examined by varying \( \frac{R_{c0}}{R_m} \) from 0.1 to 10 when both pore blockage and cake filtration are important \((\frac{t_t}{t_r} = 1)\) with no pore constriction \((\frac{t_t}{t_{\beta}} = 0)\).

The modeling results were plotted as \( \frac{d^2t}{dV^2} \) versus \( \frac{dt}{dV} \) in Figure 4.10(a1) and fraction of blocked area versus \( \frac{dt}{dV} \) in Figure 4.10(a2). It shows that all curves start with a positive slope. As increasing the value of \( \frac{R_{c0}}{R_m} \), the initial slope is approaching 2 indicating the complete pore blockage mechanism. When \( \frac{R_{c0}}{R_m} \) is quite low \((\frac{R_{c0}}{R_m} = 0.1)\), it yields a very large initial slope \((nf = 77)\). In order to get a better understanding, we plotted both \( J \) and \( -\frac{dJ}{dt} \) as function of filtration time in Figure 4.10(b1) and (b2), respectively. It shows that the flux decline rate is
increased to a maximum before the decay when \( \frac{R_{\infty}}{R_m} \) is much lower than 1. This is because the total flow rate remains almost constant during the initial filtration as the resistance of single foulant particle is very low compared to the membrane resistance.

After reaching the maximum, \( \frac{d^2 t}{dV^2} \) begins to decline, and approaches the same constant value. This is consistent with the plots of \( J \) and \( \frac{dJ}{dt} \) versus filtration time as shown in Figure 4.10(b) when the filtration time is longer than about 3000 min. It indicates that the higher resistance of single foulant particle leads to slower cake layer growth since we assume all cases share the same specific cake layer resistance (\( \frac{t_\alpha}{t_\gamma} = 1 \)). In terms of the plot in Figure 4.10(a2), the onset of cake filtration (\( nf = 0 \) at maximum \( \frac{d^2 t}{dV^2} \)) occurs when the fraction of blocked area is very close to 1 for all cases. The corresponding normalized filtration time \( \frac{t}{t_\alpha} \) is 211, and the normalized flow rate is 0.05.

### 4.4.4.2 Cake Filtration versus Pore Blockage

\( \frac{t_\alpha}{t_\gamma} \) represents the fouling rate ratio of cake filtration to pore blockage. As the value of \( \frac{t_\alpha}{t_\gamma} \) is increased, the rate of the growth of cake layer resistance will be reduced compared to the rate of blocked membrane area change. The value of \( \frac{t_\alpha}{t_\gamma} \) was varied from 0.1 to 10 while fixing \( \frac{R_{\infty}}{R_m} \) at 0.5, which is similar to the value
in Table 4.2, and $\frac{t_a}{t_\beta}$ at 0 indicating the absence of pore constriction.

In contrast to the plot in Figure 4.10, it is interesting to note that $\frac{d^2t}{dV^2}$ starts from the same value, but reaching different constant values as shown in Figure 4.11(a1). This is consistent with the fact that the initial cake layer resistance is the same ($\frac{R_{m0}}{R_m} = 0.5$) for all cases. We also note that the slope change for $\frac{t_a}{t_\gamma} = 10$ is similar to that for $\frac{R_{m0}}{R_m} = 0.1$ in Figure 4.10(a1). In the plot of $-\frac{dJ}{dt}$ versus filtration time (Figure 4.11(b2)), we can see that the rate of flux change is first increased to a maximum due to the slow cake layer growth ($\frac{t_a}{t_\gamma} = 10$) and relatively low initial resistance of single foulant particle ($\frac{R_{m0}}{R_m} = 0.5$).

The fraction of blocked membrane area at the onset of cake filtration ranges from 0.19 to 1 as $\frac{t_a}{t_\gamma}$ increasing from 0.1 to 10 (Figure 4.11(a2)). The corresponding normalized filtration time is increased from 0.21 to 498, while the normalized flow rate is reduced from 0.94 to 0.01.

In terms of this analysis, we can distinguish the results for polystyrene microspheres through PCTE and BSA through hydrophilic PVDF as shown in Figure 4.6 and Figure 4.9, respectively. Although pore blockage and cake filtration are dominant in both these systems, the pore blockage rate is larger than that of cake layer growth for polystyrene microspheres to yield a negative slope from the beginning in
Figure 4.6, while the pore blockage rate is lower than that of cake layer growth for BSA to demonstrate a positive slope first in Figure 4.9.

4.4.4.3 Pore Constriction versus Pore Blockage

The relative importance of pore constriction to pore blockage was studied by varying $\frac{t_a}{t_\beta}$ from 0.1 to 10 while keeping $\frac{R_{\infty}}{R_m}$ at 0.5, and $\frac{t_a}{t_\gamma}$ at 1. The larger the value of $\frac{t_a}{t_\beta}$ is, the slower rate for pore constriction. The calculation results were plotted in Figure 4.12(a1) as $\frac{d^2t}{dV^2}$ versus $\frac{dt}{dV}$, (a2) as fraction of blocked area versus $\frac{dt}{dV}$, (b1) as $J$ versus filtration time, and (b2) as $-\frac{dJ}{dt}$ versus filtration time.

As increasing the relative rate of pore constriction, the initial rate of filtrate flux change $-\frac{dJ}{dt}$ is increased as shown in Figure 4.12(b2) while they share the same initial filtrate flux $J$ as shown in Figure 4.12(b1). Therefore, the curve of $\frac{d^2t}{dV^2}$ versus $\frac{dt}{dV}$ for larger $\frac{t_a}{t_\beta}$ starts from higher $\frac{d^2t}{dV^2}$ (Figure 4.12(a1)). It is interesting to note that the fraction of blocked membrane area approaches lower a constant value for larger $\frac{t_a}{t_\beta}$ (Figure 4.12(a2)). As a result, although $\frac{d^2t}{dV^2}$ reaches the maximum in a short filtration time ($\frac{t}{t_a}$ ranges from 3.76 to 0.85), it keeps declining at long filtration times as shown in Figure 4.12(a1).
4.5 Conclusions

The theoretical model developed in this study accounts for three fouling mechanisms: pore blockage and cake filtration which represent external fouling, and pore constriction which represents internal fouling neglected in the previous combined fouling model. The model predictions were validated by experimental results from four designed feed-membrane combinations: polystyrene microspheres through PCTE membranes (complete external fouling); BSA solutions through hydrophobic PVDF membranes (external fouling and internal fouling); prefiltered BSA solutions through hydrophobic PVDF membranes (internal fouling); BSA solutions through hydrophilic PVDF membranes (external fouling). The experimental results are in good agreement with the modeling results. The best fit parameters for different fouling mechanisms provide deep insight into the complex fouling processes during the microfiltration, and make up the drawbacks of conventional analysis with the plot of total resistance versus filtration time or \( \frac{d^2 t}{dV^2} \) versus \( \frac{dt}{dV} \) to distinguish the fouling mechanisms.

With the scaling analysis, the characteristic times for pore blockage, pore constriction and cake filtration were defined to study the relative importance of different fouling mechanisms with the plot of \( \frac{d^2 t}{dV^2} \) versus \( \frac{dt}{dV} \). Both the transition from one fouling mechanism to another and the relative influence of each different fouling mechanism was predicted by the three-mechanism fouling model.
<table>
<thead>
<tr>
<th>Feed Solution</th>
<th>Filtration Membrane</th>
<th>Fouling Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pore blockage</td>
</tr>
<tr>
<td>I 0.25 μm PS Bead 0.2 μm PCTE (GTTP)</td>
<td>strong</td>
<td>none</td>
</tr>
<tr>
<td>II BSA 0.22 μm hydrophobic PVDF (GVHP)</td>
<td>strong</td>
<td>strong</td>
</tr>
<tr>
<td>III Prefiltered BSA 0.22 μm hydrophobic PVDF (GVHP)</td>
<td>weak</td>
<td>strong</td>
</tr>
<tr>
<td>IV BSA 0.22 μm hydrophilic PVDF (GVWP)</td>
<td>strong</td>
<td>weak</td>
</tr>
</tbody>
</table>
Table 4.2 Best Fit Fouling Parameters for Different Feed-Membrane Combinations

<table>
<thead>
<tr>
<th>Feed-Membrane Combination</th>
<th>$\alpha$ ($m^2/kg$)</th>
<th>$\beta$ ($kg^{-1}$)</th>
<th>$f^R'$ (m/kg)</th>
<th>$R_{c,0}/R_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS beads + GTTP</td>
<td>$6.3 \pm 0.3 \times 10^4$</td>
<td>0</td>
<td>$2.3 \pm 0.2 \times 10^{13}$</td>
<td>0.42</td>
</tr>
<tr>
<td>BSA + GVHP</td>
<td>$1.1 \pm 0.2 \times 10^{-1}$</td>
<td>127.6 ± 0.2</td>
<td>$7.0 \pm 0.3 \times 10^{10}$</td>
<td>0.93</td>
</tr>
<tr>
<td>Prefiltered BSA + GVHP</td>
<td>$3.8 \pm 0.2 \times 10^{-3}$</td>
<td>192.3 ± 0.2</td>
<td>$6.9 \pm 0.2 \times 10^{9}$</td>
<td>0.28</td>
</tr>
<tr>
<td>BSA + GVWP</td>
<td>$2.9 \pm 0.2 \times 10^{-1}$</td>
<td>$86.4 \pm 0.3 \times 10^{-2}$</td>
<td>$1.9 \pm 0.1 \times 10^{10}$</td>
<td>0.84</td>
</tr>
</tbody>
</table>
Table 4.3 Definitions of Characteristic Time for Different Fouling Mechanisms

<table>
<thead>
<tr>
<th>Fouling Mechanism</th>
<th>Based on fouling parameters</th>
<th>Based on initial fouling rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore blockage</td>
<td>$t_{\alpha} = \frac{1}{\alpha J_0 C_b}$</td>
<td>$\frac{1}{t_{\alpha}} = \frac{dA_m}{dt}_{t=0} = \frac{1}{A_m}$</td>
</tr>
<tr>
<td>Pore constriction</td>
<td>$t_{\beta} = \frac{1}{\beta Q_0 C_b}$</td>
<td>$\frac{1}{t_{\beta}} = \frac{dV_{mp}}{dt}<em>{t=0} = \frac{1}{V</em>{mp}}$</td>
</tr>
<tr>
<td>Cake filtration</td>
<td>$t_{\gamma} = \frac{R_n}{fR'J_0 C_b}$</td>
<td>$\frac{1}{t_{\gamma}} = \frac{dR_n}{dt}_{t=0} = \frac{1}{R_m}$</td>
</tr>
<tr>
<td></td>
<td>PS Beads + PCTE$^{[1]}$</td>
<td>BSA + GVHP$^{[2]}$</td>
</tr>
<tr>
<td>----------------</td>
<td>------------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>$t_\alpha$ (min)</td>
<td>1</td>
<td>489</td>
</tr>
<tr>
<td>$t_\beta$ (min)</td>
<td>$\infty$</td>
<td>1088</td>
</tr>
<tr>
<td>$t_\gamma$ (min)</td>
<td>110</td>
<td>35</td>
</tr>
</tbody>
</table>

[1]. $C_b = 0.001 \text{ g/L}$, $Q_o = 1.2 \times 10^{-7} \text{ m}^3/\text{s}$, $A_m = 3.9 \times 10^{-4} \text{ m}^2$

[2]. $C_b = 1 \text{ g/L}$, $Q_o = 1.2 \times 10^{-7} \text{ m}^3/\text{s}$, $A_m = 3.9 \times 10^{-4} \text{ m}^2$
Figure 4.1 Schematic diagram for all three mechanisms including pore blockage, pore constriction, and cake filtration.
Figure 4.2 Filtration of 0.25 μm polystyrene microsphere solutions through a 0.2 μm PCTE membrane (GTTP): a) normalized flow rate versus filtration time b) total resistance versus filtration time. Solid curves are model calculations based on the best fit parameters listed in Table 4.2.
Figure 4.3 Filtration of BSA solutions through a 0.22 µm hydrophobic PVDF membrane (GVHP): a) normalized flow rate versus filtration time b) total resistance versus filtration time. Solid curves are model calculations based on the best fit parameters listed in Table 4.2.
Figure 4.4 Filtration of prefiltered BSA solutions through a 0.22 µm hydrophobic PVDF membrane (GVHP): a) normalized flow rate versus filtration time b) total resistance versus filtration time. Solid curves are model calculations based on the best fit parameters listed in Table 4.2.
Figure 4.5 Filtration of BSA solutions through a 0.22 µm hydrophilic PVDF membrane (GVWP): a) normalized flow rate versus filtration time b) total resistance versus filtration time. Solid curves are model calculations based on the best fit parameters listed in Table 4.2.
Figure 4.6 $d^2t/dV^2$ versus $dt/dV$ analysis for 0.25 µm polystyrene microsphere solutions filtered through a 0.2 µm PCTE membrane (GTTP). Solid curves are model calculations based on the best fit parameters listed in Table 4.2.
Figure 4.7 $d^3t/dV^2$ versus $dt/dV$ analysis for BSA solutions filtered through a 0.22 µm hydrophobic PVDF membrane (GVHP). Solid curves are model calculations based on the best fit parameters listed in Table 4.2.
Figure 4.8 $d^2t/dV^2$ versus $dt/dV$ analysis for prefiltered BSA solutions filtered through a 0.22 µm hydrophobic PVDF membrane (GVHP). Solid curves are model calculations based on the best fit parameters listed in Table 4.2.
Figure 4.9 $d^2l/dV^2$ versus $dt/dV$ analysis for BSA solutions filtered through a 0.22 µm hydrophilic PVDF membrane (GVWP). Solid curves are model calculations based on the best fit parameters listed in Table 4.2.
Figure 4.10 Theoretical analysis of the effect of $R_{co}/R_m$ on flux decline based on the three-mechanism fouling model.
Figure 4.11 Theoretical analysis of the effect of \( t_\alpha/t_\gamma \) on flux decline based on the three-mechanism fouling model.
Figure 4.12 Theoretical analysis of the effect of $t_\alpha /t_\beta$ on flux decline based on the three-mechanism fouling model.
CHAPTER 5 Theoretical Analysis of the Effects of Asymmetric Membrane Structures on External Fouling

5.1 Introduction

Most of these previous fouling models assumed that filtration membrane were composed of an array of straight-through cylindrical pores. Ho and Zydney [124] developed a mathematical model accounting for the effects of membrane morphology on the fouling processes. In this model, the pore connectivity was characterized by the permeability ratio in the horizontal direction to that in the transverse direction which could be measured by independent experiments [125]. This model successfully simulated the flux decline during the filtration through the membranes with highly interconnected pore structure [131]. Jackson et al. [229] also related the membrane structure to transport phenomena in an effort to improve the understanding of the microfiltration or ultrafiltration processes by using a stochastic model to describe the pore geometric properties. Although all these models accounted for the lateral flow within the membrane structure, the membranes were treated as homogeneous or symmetric porous structures.

Traditionally, commercial microfiltration membranes have homogeneous structures. However, there is increasing use of asymmetric and composite membranes. In contrast to symmetric membranes, asymmetric membranes usually have a very thin skin layer that determines the membrane selectivity and a relatively
thick porous supporting layer [230]. Asymmetric membranes can have better performance than symmetric membranes in that the retentive layer in an asymmetric membrane can be thinner, thereby reducing the total membrane resistance relative to a symmetric membrane of similar retentive capability. Highly asymmetric membranes with pores gradually decreasing in size from the feed side to the permeate side and membranes having layers of different porosity also have been manufactured [231-233]. Ulbricht et al. [132] prepared a novel polyethersulfone (PES) membrane named DuraPES® with a gradient pore size profile, and this novel membrane shows significantly lower fouling tendency than the other membranes. Chae et al. [234] compared the process performance and membrane fouling characteristic of both symmetric and asymmetric PVDF membranes, and found that the asymmetric PVDF membrane is more resistant to membrane fouling than the symmetric membrane.

Composite membranes combine two or more layers into a single membrane, and each layer is formed independently with isotropic or anisotropic morphology. This will provide additional degrees of freedom to develop membrane structures that are able to meet the unique fouling characteristics [235]. Kools [236] invented a method of producing an integral multilayered porous membrane by simultaneously co-casting a plurality of polymer solutions onto a support to form a multilayered liquid sheet and form a porous membrane through phase separation. Various experimental studies [119, 120, 237, 238] revealed that composite membranes have better fouling resistance than homogeneous membranes. However, most of these studies simply attributed the improvement of performance to the modification of the
membrane hydrophobicity. In addition, it was reported that the reversed membrane orientation, i.e., supporting layer facing the feed stream, could reduce the extent of fouling during the normal flow filtration [136, 137, 239].

Although a considerable number of asymmetric or composite membranes with better fouling resistance have been commercially manufactured, it is not clearly understood on a fundamental level how the asymmetric membrane structures affect the flux decline behavior during the filtration. Ho and Zydney [130, 131] developed a mathematical model accounting for fluid flow through composite membranes formed with two layers: an upper layer with noninterconnected pores, and a substrate with interconnected pores. However, it is difficult to apply this model to describe membranes with a varying degree of pore connectivity throughout the membrane.

The objective of this study was to develop a mathematical description of flux decline behavior for membranes with various asymmetric structures. The asymmetric structure was characterized by the radial and axial permeabilities within the membrane, which were varied in the transverse direction to simulate composite membranes. The modeling was then compared with the experimental flux decline data during dead end filtration of polystyrene microsphere solutions and BSA solutions through pseudo-composite membranes composed of two homogeneous membranes with different pore connectivity or hydraulic resistance.
5.2 Model Development

The assumptions for the characteristic region of the fouled membrane in Ho and Zydney’s work [124] were employed for our current study. It was assumed that the foulant particles deposit uniformly and randomly over the membrane surface so that the entire fouled membrane could be characterized by a cylindrical region with the blocked area (central blockage model as shown in Figure 1.6(a)) or open area (central void model as shown in Figure 1.6(b)) at the center.

The central blockage model describes the initial fouling with low surface coverage, while the central void model is applied to the highly fouled membrane during the long time filtration. The relationships between the fraction of blocked area $\theta$ and the characteristic size of the blocked area ($r_{\text{blocked}}$ for the central blockage model, $r_{\text{open}}$ for the central void model) were given by Eqs. (1.29) and (1.30).

Combining Darcy’s Law and the continuity equation, we can determine the pressure distribution within the membrane structures with the governing equation (Eq. (5.1)) and the corresponding boundary conditions (Eqs. (5.2) to (5.6)):

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r k \frac{\partial p}{\partial r} \right) + \frac{\partial}{\partial z} \left( k \frac{\partial p}{\partial z} \right) = 0 \quad (5.1)
\]

\[
\frac{\partial p}{\partial r} = 0 \quad \text{at} \ r = 0 \quad (5.2)
\]

\[
\frac{\partial p}{\partial r} = 0 \quad \text{at} \ r = r_c \quad (5.3)
\]
central blockage \[ \begin{cases} \frac{p_f - p}{\mu(R_z + R_{z,0})} = -k_z \frac{\partial p}{\partial z} & 0 \leq r \leq r_{\text{blocked}} \\ p = p_f & r_{\text{blocked}} < r \leq r_c \end{cases} \] at \( z = 0 \) \hspace{1cm} (5.4)\\

central void \[ \begin{cases} p = p_f & 0 \leq r < r_{\text{open}} \\ \frac{p_f - p}{\mu(R_z + R_{z,0})} = -k_z \frac{\partial p}{\partial z} & r_{\text{open}} \leq r \leq r_c \end{cases} \] at \( z = 0 \) \hspace{1cm} (5.5)\\

\[ p = p_p \] at \( z = L_m \) \hspace{1cm} (5.6)

where \( k_r \) and \( k_z \) are the Darcy permeabilities in the radial and transverse directions, respectively. Membranes with straight-through pores can be modeled with \( \frac{k_r}{k_z} = 0 \), whereas those with highly interconnected pores have \( \frac{k_r}{k_z} \approx 1 \). In earlier studies, a constant permeability ratio of \( k_r \) to \( k_z \) was used to describe symmetric membrane structures. In order to simulate asymmetric membrane structures mathematically, the permeabilities here were related to the position in the transverse direction.

In the boundary conditions, \( p_f \) is the pressure of the feed solution, \( p_p \) is the pressure of the permeate, \( L_m \) is the thickness of the entire membrane, \( R_z \) is the resistance of the cake layer, and \( R_{z,0} \) is the initial resistance of the single foulant particle. We note that the Dirichlet conditions were applied for the open area, whereas the Robin conditions were applied to the blocked area indicating the flux balance at the interface between membrane surface and cake layer.

The governing equation (5.1) was normalized to get a dimensionless form:

\[ \frac{1}{r^*} \frac{\partial}{\partial r^*} \left( r^* K_z K \frac{\partial p^*}{\partial r^*} \right) + \frac{\partial}{\partial z^*} \left( K \frac{\partial p^*}{\partial z^*} \right) = 0 \] \hspace{1cm} (5.7)
where \( r^* = \frac{r}{r_{\text{blocked}}} \), \( z^* = \frac{z}{L_m} \), and \( p^* = \frac{p - p_p}{p_f - p_p} \). \( K_z \) is the dimensionless permeability in the transverse direction:

\[
K_z(z^*) = \frac{k_z(z^*)}{k_z(z^* = 0)}
\] (5.8)

This parameter characterizes the variation of the membrane hydraulic resistance in the transverse direction. \( K \) is the normalized permeability ratio which is defined as:

\[
K(z^*) = \left( \frac{L_m}{r_{\text{blocked}}} \right)^2 \frac{k_r}{k_z}
\] (5.9)

Varying \( K \) along the \( z \) direction will change the pore connectivity to form various asymmetric membranes. This partial differential equation (PDE) with variable coefficient can be solved numerically by combining the finite volume method and multigrid method (FV-MG method) as described in Appendix C.2.

In order to evaluate the filtrate flux as a function of filtration time, it was required to describe the rate of blocked area change and the rate of cake layer growth for the specified boundary conditions and the governing equation (5.1) for any filtration time. Here, we assumed that pressure profile achieved steady state instantly during the filtration. In the current model, we only accounted for the effects of external fouling, including both pore blockage and cake filtration.

In terms of the pore blockage model, the rate of blocked area change can be determined by:

\[
\frac{dA_b}{dt} = \alpha \bar{T} v A_c C_b
\] (5.10)
As introduced in previous sections, $\alpha$ is the pore blockage parameter representing the blocked membrane area per unit mass of foulant particles. In an earlier study [128], it was reported that $\alpha$ can be related to the particle size $r_p$, membrane pore size $r_m$, and membrane surface porosity $\varepsilon_{ms}$ by:

$$
\alpha = \frac{1}{\varepsilon_{ms}} \left( \frac{r_m}{r_p} \right)^2 \alpha'
$$

(5.11)

where $\alpha'$ is defined as the projected area of the foulant particles per unit mass of foulant particle, and it is independent of the properties of the membrane. $J_u$ is the average fluid flux within the open area, and it is a function of both the fraction of blocked area $\theta$ and the resistance ratio of the cake layer to the membrane $\frac{R_c + R_{c0}}{R_m}$.

We can evaluate $J_u$ by numerically integrating the pressure gradient within the open area on the membrane surface:

$$
J_u = -\frac{2\pi \int_{r_{Blocked}}^{r_c} k \frac{\partial p}{\partial z} \bigg|_{z=0} rdr}{(1-\theta)\pi r_c^2}
$$

(5.12)

$$
J_u = -\frac{2\pi \int_{0}^{r_{spec}} k \frac{\partial p}{\partial z} \bigg|_{z=0} rdr}{(1-\theta)\pi r_c^2}
$$

(5.13)

Eqs. (5.12) and (5.13) are applied for the central blockage model and central void model, respectively.

The cake layer growth is reflected by the rate of cake layer resistance change within the blocked area. Here, we implicitly assume that the cake layer is uniform since the cake layer growth is self-leveling process. As described by the cake
filtration model, the rate of cake layer resistance change can be determined by:

$$\frac{dR_c}{dt} = f' R' J_b C_h$$  \hspace{1cm} (5.14)

where $f'$ is the mass fraction of the foulant particles in the feed solution, and $R'$ is the specific cake layer resistance, which is assumed to be constant during a constant pressure filtration. Previous studies [75, 240] showed that $R'$ was a function of the transmembrane pressure $\Delta p$ due to the compressibility of the foulant deposit:

$$R' = k_p \left( \frac{\Delta p}{1 N/m^2} \right)^{S_c}$$  \hspace{1cm} (5.15)

where the value of compressibility parameter $S_c$ ranges from 0 for an incompressible cake layer to 1 for a very highly compressible cake layer. $J_b$ is the average fluid flux within the blocked area, like $J_u$, it is also a function of both the fraction of blocked area $\theta$ and the resistance ratio of the cake layer to the membrane $\frac{R_c + R_{c0}}{R_m}$. We can evaluate $J_b$ with Eqs. (5.16) and (5.17) for the central blockage model and central void model, respectively:

$$J_b = \frac{2\pi \int_{r_{u0}}^{r_c} k_z \left. \frac{\partial p}{\partial z} \right|_{z=0} rdr}{\theta \pi r_c^2}$$  \hspace{1cm} (5.16)

$$J_b = \frac{2\pi \int_{r_{u0}}^{r_c} k_z \left. \frac{\partial p}{\partial z} \right|_{z=0} rdr}{\theta \pi r_c^2}$$  \hspace{1cm} (5.17)

The total flow rate is the linear combination of the flow rates within the blocked area and the open area. The normalized flow rate can be given in terms of the dimensionless form (Eq. (5.7)) as:
\[
\frac{Q}{Q_0} = -2 \int_0^1 K(z^*) dz^* \cdot \left[ \int_0^1 \frac{dp^*}{dz^*} \right]_{z^*=0} r^* dr^*
\]  
(5.18)

The first integral in Eq. (5.18) denotes the total resistance of the clean membrane, and the second integral represents the flow rate of the fouled membrane.

### 5.3 Experimental Methods

#### 5.3.1 Materials

In this study, both 0.25 \( \mu m \) polystyrene microspheres and BSA solutions were employed as foulants for modeling validation. All solutions were freshly prepared before each experiment following the procedure introduced in sections 3.2.1 and 3.2.2.

The membranes used in this study include two PCTE membranes (0.1 \( \mu m \) VCTP, 0.2 \( \mu m \) GTTP), and a series of hydrophilic PVDF membranes with nominal pore size ratings (0.1 \( \mu m \) VVLP, 0.22 \( \mu m \) GVWP, 0.45 \( \mu m \) HVLP). The detailed information for these membranes was listed in Table 3.2.

#### 5.3.2 Filtration Experiments

The common performance of filtration experiment was introduced in section 3.3.1. The transmembrane pressure \( \Delta p \) was varied from 2 to 12 psi for different membranes or membrane combinations.

Polystyrene microspheres and BSA solutions were filtered through both
0.1 \mu m PCTE membranes and 0.1 \mu m PVDF membranes to determine the fouling parameters and parameters for the membrane morphology. The effects of pore connectivity on the flux decline were examined by filtering both the polystyrene microspheres and BSA solutions through the pseudo-composite membranes composed of 0.2 \mu m PCTE membrane and 0.1 \mu m PVDF membrane. The pseudo-composite membranes with 0.1 \mu m PVDF membrane on the top layer while varying the pore size of the PVDF membranes on the bottom layer from 0.1 to 0.45 \mu m were employed to validate the effects of varying membrane resistance on the flux decline. In each filtration experiment, the concentration of polystyrene microsphere solutions was varied from 0.00125 to 0.01 g/L; the concentration of BSA solutions was varied from 1 to 4 g/L.

Before the flux decline measurements, all membranes were tested with DI water to characterize the permeability in the transverse direction \( k_z \). In particular, for the double-layer membranes, the hydraulic permeability for both layers was tested before and after the flux decline measurements. The procedures for measuring the hydraulic permeability were introduced in section 3.3.2.3.

5.3.3 Determine Compressibility Parameter

In terms of Eq. (5.15), we can get the linear form for the compressibility parameter \( S_c \):

\[
\ln \left( R_{\text{total}} - R_m - R_c \right) = S_c \ln \left( \frac{\Delta p}{1 \text{N/m}^2} \right) + \ln k_p m_p \tag{5.19}
\]
In order to fit $S_z$, 0.2 $\mu m$ PCTE were fouled by 0.00125 g/L polystyrene microsphere solution or 1 g/L BSA solution for 2 $h$. Then, these fouled membranes were used to measure the hydraulic resistance under transmembrane pressures varying from 2 to 12 psi.

### 5.4 Theoretical Analysis of Optimizing Asymmetry

In this section, we applied the modified fouling model to optimizing the asymmetric structures of composite membranes composed of two layers with different pore connectivity ($K = \left(\frac{L_{m}}{r_{\text{blocked}}} \right)^2 \frac{k_r}{k_z}$) or hydraulic resistance ($R_m = \frac{L_{m}}{\mu k_z}$). Here, we assumed that the top layer and the bottom layer of the composite membranes had the same thickness ($L_{\text{top}} = L_{\text{bottom}}$).

In terms of the dimensionless form of the governing equation (5.7), there are three degrees of freedom for the double-layer composite membranes: $K_{\text{top}}$ (indicating the pore connectivity of the top layer), $K_{\text{bottom}}$ (indicating the pore connectivity of the bottom layer), and $K_{\text{bottom}}$ (indicating the hydraulic resistance ratio of top layer to bottom layer $\frac{R_{\text{top}}}{R_{\text{bottom}}}$). Hence, we studied the effects of these parameters on the flux decline by fixing one parameter while varying the other two at the same time. It was also assumed that the fraction of the blocked area was equal to 0.64, and the blocked region was located at the center of the characteristic cylindrical region (central blockage model). Two different cases were studied in terms of the
relative permeability of the cake layer to membrane.

In the first case, the cake layer was assumed impermeable. We fixed $K_{\text{bottom}}$ at 0.01, 1, and 100 while varying both $K_{\text{top}}$ and $\frac{R_{\text{mop}}}{R_{\text{mbottom}}}$ from 0.01 to 100 continuously. On the other hand, we kept $K_{\text{top}}$ at 0.01, 1, and 100 as changing $K_{\text{bottom}}$ and $\frac{R_{\text{mop}}}{R_{\text{mbottom}}}$ in the same manner. Figure 5.1 shows the grayscale plot for the normalized flow rate $\frac{Q}{Q_0}$ as a function of both $K_{\text{top}}$ (or $K_{\text{bottom}}$) and $\frac{R_{\text{mop}}}{R_{\text{mbottom}}}$. The deeper grayscale denotes the region with lower normalized flow rate. The dashed lines indicate the contour of $k_{\text{top}}$, $k_{\text{bottom}}$. In the log-log plot for both $K_{\text{top}}$ (or $K_{\text{bottom}}$) and $\frac{R_{\text{mop}}}{R_{\text{mbottom}}}$, the contour of $\frac{k_{\text{top}}}{k_{\text{bottom}}}$ is an array of parallel straight lines with slope of 1 ($K_{\text{bottom}}$ = constant) or −1 ($K_{\text{top}}$ = constant).

In Figure 5.1(a), it can be seen that the normalized flow rate is increased as increasing $K_{\text{top}}$ and decreasing $\frac{R_{\text{mop}}}{R_{\text{mbottom}}}$ when $K_{\text{bottom}}$ is constant. The composite membranes have relatively low normalized flow rate for lower $K_{\text{bottom}}$ than those for higher $K_{\text{bottom}}$. When we keep $K_{\text{top}}$ constant in Figure 5.1(b), the change of $\frac{R_{\text{mop}}}{R_{\text{mbottom}}}$ affected the normalized flow rate in the similar manner, while varying $K_{\text{bottom}}$ had little impact on the normalized flow rate.

For the permeable cake layer (or relatively low resistance ratio of cake layer to membrane), the resistance ratio of cake layer to top layer membrane, which is
involved in the Robin boundary conditions for the blocked area (Eqs. (5.4) and (5.5)), was changed by varying both $k_{\text{top}}$ and $k_{\text{bottom}}$ to keep the total membrane resistance constant. The relationship between $k_{\text{top}}$ and $\frac{R_{\text{mtop}}}{R_{\text{mbottom}}}$ for constant $R_{\text{mtotal}}$ can be given by:

$$k_{\text{top}} = \frac{L_m}{2\mu R_{\text{mtotal}}} \left(1 + \frac{1}{\frac{R_{\text{mtop}}}{R_{\text{mbottom}}}}\right)$$  \hspace{1cm} (5.20)

The calculation results for a permeable cake layer were plotted in Figure 5.2(a) for constant $K_{\text{bottom}}$ and (b) for constant $K_{\text{top}}$. The resistance ratio of cake layer to the total membrane was set to 0.5. It shows that the normalized flow rate is affected by both $K_{\text{top}}$ (or $K_{\text{bottom}}$) and $\frac{R_{\text{mtop}}}{R_{\text{mbottom}}}$ in the similar manner as shown by the case of impermeable cake layer (Figure 5.1). However, the extent of normalized flow rate change as increasing $\frac{R_{\text{mtop}}}{R_{\text{mbottom}}}$ is decreased in that the relative resistance of cake layer to the top layer membrane is decreased (Eq. (5.20)).

In order to provide deep insight into the interplay between $k_z$ and $k_z$ on the flux decline, we chose Figure 5.1(a2), in which the normalized flow rate was significantly changed in each direction, as a template, and studied the effects of the different asymmetric structures along various contours on the flux decline with the plots of both pressure profile and flow streamline. The normalized pressure profile was directly obtained from the calculation results of the dimensionless form of governing equation (5.7). The flow streamlines was obtained by numerically solving
the streamline function:

\[
\frac{dr^*}{dz^*} = K \frac{\partial p^*}{\partial z^*}
\]  

(5.21)

5.4.1 Effects of Varying \( k_r \) on Flux Decline

First, we varied \( k_r \) while keeping \( k_z \) constant by choosing three representative points over the contour of \( \frac{k_{\text{bottom}}}{k_{\text{top}}} = 1 \) (\( \frac{R_{\text{top}}}{R_{\text{bottom}}} = 1 \)) in Figure 5.1(a2). As moving over the contour of \( \frac{k_{\text{bottom}}}{k_{\text{top}}} = 1 \) from left to right, the value of \( k_{\text{top}} \) was increased, thereby larger \( K_{\text{top}} \). We calculated the normalized flow rate as a function of fraction of blocked area as shown in Figure 5.3. It shows that the composite membrane with lower pore connectivity in the top layer (red curve, \( \frac{k_{\text{top}}}{k_{\text{top}}} = 0.01 \)) yields a lower normalized flow rate for the whole coverage range compared to the symmetric membrane (black curve). When the value of \( k_{\text{top}} \) is 100 times as large as \( k_{\text{top}} \), the normalized flow rate is significantly increased as shown by blue curve.

In Figure 5.4, the normalized pressure profile (a) and the flow streamline (b) were plotted for these three representative membrane structures with different pore connectivity in the top layer while keeping \( K_{\text{bottom}} = 1 \). When the composite membrane has relatively low pore connectivity in the top layer (\( \frac{k_{\text{top}}}{k_{\text{top}}} = 0.01 \)), the pressure drop is constrained within the open area on the top layer (Figure 5.4(a1)). As a result, the lateral flow in the top layer is limited to a small region around the
brim of the blocked area (Figure 5.4(b1)). However, as $k_z$ is increased 100 times on the bottom layer, the flow streamlines go farther in the radial direction yielding a discontinuity at the interface between the top layer and the bottom layer. In contrast, when the top layer has large pore connectivity ($\frac{k_{\text{top}}}{k_{z\text{top}}} = 100$) compared to the bottom layer ($\frac{k_{\text{bot}}}{k_{z\text{bot}}} = 1$), it yields a nearly uniform pressure gradient for both the blocked area and open area (Figure 5.4(a3)). Therefore, the radial flow occurs only beneath the cake layer (Figure 5.4(b3)).

5.4.2 Effects of Varying $k_z$ on Flux Decline

In the second case, we varied $k_z$ while fixing $\frac{k_{\text{top}}}{k_{z\text{top}}} = 1$. This is equivalent to moving over the diagonal indicating $\frac{k_{\text{top}}}{k_{z\text{top}}} = 1$ from the bottom left to the upper right by decreasing $k_{z\text{top}}$ while keeping the other dimensionless constant parameters (Figure 5.5). It is interesting to note that, in this case, both pore connectivity ($\frac{k_{\text{top}}}{k_{z\text{top}}}$) and hydraulic resistance ($k_{z\text{top}}$) were changed simultaneously with decreasing $k_{z\text{top}}$.

Figure 5.5 shows the normalized flow rate versus the fraction of blocked area for three composite membranes with various $k_{z\text{top}}$. It demonstrates that the composite membrane with lower $k_{z\text{top}}$ (red curve) has higher normalized flow rate than that of symmetric membrane (black curve). Although the relative pore
connectivity $\frac{k_{\text{top}}}{k_{\text{ztop}}}$ in the top layer is higher with decreasing $k_{\text{ztop}}$, the effect of the relative membrane resistance is dominant when $\frac{k_{\text{top}}}{k_{\text{ztop}}}$ is smaller than $\frac{k_{\text{bottom}}}{k_{\text{zbottom}}}$. As $k_{\text{ztop}}$ is decreased to an even smaller value ($\frac{k_{\text{top}}}{k_{\text{ztop}}} = \frac{k_{\text{bottom}}}{k_{\text{zbottom}}} = 100$, blue curve), the pore connectivity is dominant, thereby a higher normalized flow rate compared to symmetric membrane (black curve).

For a better understanding, we compared these composite membranes in the plots of normalized pressure profile and flow streamlines (Figure 5.6). For the composite membrane with larger $k_{\text{ztop}}$, the pressure drop is concentrated within the bottom layer as the bottom layer has higher hydraulic resistance as shown in Figure 5.6(a1). Although the top layer has relatively low pore connectivity ($\frac{k_{\text{top}}}{k_{\text{ztop}}} = 0.01$), the fluid dramatically flows into the blocked area as indicated by the flow streamlines in Figure 5.6(b1). This is due to the fact that the fluid is always able to find the path with the lowest resistance by itself. Increasing the lateral flow will enlarge the effective cross-section area in the direction normal to the membrane surface, thereby a lower hydraulic resistance. For the composite membrane with lower $k_{\text{ztop}}$, the pressure gradient is constrained within the top layer for both the blocked and open areas (Figure 5.6(a3)). Similar to the results in Figure 5.4(a3), the fluid flows in the radial direction only beneath the cake layer since the pore connectivity in the top layer is much larger than that on the bottom layer (Figure 5.6(b3)).
5.4.3 Effects of Varying Both $k_r$ and $k_z$ on Flux Decline

By moving over the contour of $K_{top} = 1$ in Figure 5.1(a2) from the bottom to the top, both $k_r$ and $k_z$ are decreased (top layer) or increased (bottom layer) on the same scale to keep $\frac{k_{z_{top}}}{k_{z_{top}}} = \frac{k_{z_{bottom}}}{k_{z_{top}}} = 1$. This case represents the composite membranes have the uniform pore connectivity for both layers but different hydraulic resistance.

In Figure 5.7, we can see that the composite membrane with lower resistance in the bottom layer (blue curve) has a lower normalized flow rate compared to the symmetric membrane (black curve), while the normalized flow rate of the composite membrane with larger resistance in the bottom layer (red curve) is much higher than that of the symmetric membrane.

In the corresponding plots of normalized pressure profile and flow streamlines (Figure 5.8), it is demonstrated that the pressure drop is almost completely concentrated within the bottom layer for the composite membrane with higher resistance in the bottom layer ($\frac{k_{z_{bottom}}}{k_{z_{top}}} = 0.01$) as shown in Figure 5.8(a1). Therefore, although the bottom layer has the same pore connectivity as the top layer ($\frac{k_{r_{top}}}{k_{z_{top}}} = \frac{k_{z_{bottom}}}{k_{z_{top}}} = 1$), it seems that the fluid prefers to find the path in the radial direction on the top layer other than in the bottom layer since $k_{r_{top}}$ is much larger than $k_{r_{bottom}}$ (Figure 5.8(b1)). When the top layer has higher resistance
(\frac{k_{\text{bottom}}}{k_{\text{top}}} = 100), significant radial flow is demonstrated in the top layer, but it goes slightly farther in the bottom layer due to the increase of \( k_r \).

In conclusion, the highly interconnected pore structure can help the fluid to flow into the blocked area to alleviate the fouling during the filtration, and the variation of pore connectivity in the top layer of the composite membrane has more significant impact of the flux decline compared to the bottom layer. In the other hand, the fluid tends to enlarge the cross-sectional area in the transverse direction when \( k_r \) is larger than \( k_z \), and the composite membrane with the higher resistance in the bottom layer has higher lateral flow in the top layer, thereby resulting in slower flux decline.

### 5.5 Experimental Results and Model Validation

In order to validate the modeling predictions, we simulated the composite membranes by using the pseudo-composite membranes composed of two homogeneous membranes with different pore connectivity and hydraulic resistance. The results of flux decline measurements were compared to the modeling results.

#### 5.5.1 Model Parameters

The external fouling parameters (\( \alpha \) for pore blockage, \( fR' \) and \( R_{e0} \) for cake filtration) were obtained from the filtration experiments with membranes having straight-through pores. Then, the membranes with highly interconnected pores
(0.1 \mu m \text{ PVDF}) were used to filter the same solution so that the parameters for membrane morphology \((K = \left( \frac{L_m}{r_{\text{blocked}}} \right)^2 \frac{k_r}{k_z})\) could be determined.

First, solutions of 0.25 \mu m polystyrene microspheres, with concentrations from 0.000625 to 0.005 g/L, were filtered through 0.1 \mu m PCTE membranes under a constant pressure of 20 psi as shown in Figure 5.9(a). The initial filtrate flux ranged from 2.3 \times 10^{-4} to 2.5 \times 10^{-4} m/s. Then, the external fouling parameters were fit based on the combined fouling model developed by Ho and Zydney [75] as listed in Table 5.1. The solid curves in Figure 5.9(a) are the model calculations using the best fit parameters in Table 5.1. Clearly, the fitting results are in good agreement with the experimental results across the entire range of microsphere concentrations.

The experimental data of 0.25 \mu m polystyrene microspheres filtering through 0.1 \mu m PVDF membrane were plotted in Figure 5.9(b). The transmembrane pressure was set to 6 psi to keep the initial filtrate flux ranging from 2.7 \times 10^{-4} to 3.1 \times 10^{-4} m/s. Note that the 0.1 \mu m PVDF membrane was chosen to test the flux decline measurements instead of 0.22 \mu m PVDF membrane. This is because the porous PVDF membranes have a relatively broad pore size distribution compared to PCTE membranes with the same nominal pore size rating. The PVDF membranes with the nominal pore size (0.22 \mu m) close to the particle size (0.25 \mu m) may not be able to reject all particles on the membrane surface.

Based on the external fouling parameters from the PCTE membranes, the
normalized permeability ratio $K$ for porous PVDF membranes can be determined by fitting the experimental data from $0.1 \mu m$ PVDF membrane based on the fouling model accounting for the membrane morphology. The best fitting $K$ for polystyrene microspheres filtering through $0.1 \mu m$ PVDF membrane is 0.9. The modeling calculations based on the best fitting parameters were plotted as solid curves in Figure 5.9(b). It is interesting to note that $0.1 \mu m$ PCTE membranes have lower flux decline compared to $0.1 \mu m$ PVDF membranes. This is due to two opposing factors influencing the flux decline behavior of PCTE and PVDF membranes. First, the highly interconnected pore structure allows the fluid to flow around and under the blockage to alleviate the fouling. On the other hand, increasing the resistance ratio of the cake layer to membrane yields higher normalized flow rate. Although the $0.1 \mu m$ PCTE membrane has the noninterconnected pore structure, its hydraulic membrane resistance is much higher than that of $0.1 \mu m$ PVDF membranes resulting in a relatively low flux decline.

The same experiments were performed with BSA solutions. The concentration of BSA solutions ranged from 0.5 to $4 g/L$. The experimental results were plotted in Figure 5.10 (a) for $0.1 \mu m$ PCTE membrane and (b) for $0.1 \mu m$ PVDF membrane. The best fitting external fouling parameters from the BSA solution through the $0.1 \mu m$ PCTE membrane were included in Table 5.1. The best fit $K$ for the BSA solution through the $0.1 \mu m$ PVDF membrane is determined as 0.85, which is slightly lower than the value from polystyrene microspheres. This discrepancy is likely due to the broad particle size distribution of
protein aggregates. All modeling calculations were plotted as solid curves in Figure 5.10.

In terms of Eq. (5.19), the compressibility parameter \( S_c \) can be determined by linearly fitting the experimental data of \( \ln \left( R_{\text{total}} - R_m - R_{c0} \right) \) versus \( \ln \left( \frac{\Delta p}{1N/m^2} \right) \). The experimental results were plotted in Figure 5.11(a) for polystyrene microspheres and (b) for BSA. Linear fitting results show that the values of \( S_c \) are \( 0.21 \pm 0.03 \) for polystyrene microspheres and \( 0.37 \pm 0.04 \) for BSA. Note that the experimental value of \( S_c \) for the polystyrene microspheres is larger than zero, which is the theoretical value for incompressible particles. This is likely due to the tighter packing and stronger interaction between the microspheres and membrane surface under higher performance pressure.

5.5.2 Model Validation

To validate the theoretical analysis, we formed composite membranes by placing one membrane directly on top of another membrane having different pore connectivity or membrane resistance.

5.5.2.1 Effects of Pore Connectivity

The effects of the variation of pore connectivity on the flux decline were validated by filtering both 0.25 \( \mu m \) polystyrene microspheres and BSA solutions through the pseudo-composite membranes, which were composed of a 0.2 \( \mu m \) PCTE membrane (straight-through pores) and a 0.1 \( \mu m \) PVDF membrane (highly
interconnected pores. The same filtration measurements were repeated with a reversed arrangement.

Figure 5.12(a) shows the flux decline data for 0.00125 g/L 0.25 μm polystyrene microspheres filtered through a 0.2 μm PCTE membrane, 0.1 μm PVDF membrane, and the double-layer membranes composed of 0.2 μm PCTE and 0.1 μm PVDF membranes. The transmembrane pressure varied from 2 to 8 psi for different membranes and membrane combinations so that the initial filtrate flux could be limited around $3 \times 10^{-4}$ m/s. It shows that the composite membrane with the PVDF membrane on top of the PCTE membrane yielded lower flux decline compared to the composite membrane with the reversed orientation. Each layer of the composite membrane was tested for hydraulic permeability before and after the flux decline measurements. Figure 5.12(b) shows the ratio of initial permeability and final permeability for both top and bottom layers. The permeability of the bottom layer retained more than 90% of the initial value after the filtration. This indicates that external fouling was dominant during the filtration processes with most of the fouling occurring at the top layer regardless of the membrane used in top layer.

Similarly, the same flux decline measurements were done using BSA solutions. Figure 5.13(a) shows the flux decline for 1 g/L BSA solutions filtering through the same single layer membranes and double-layer membranes used for polystyrene microspheres. When the porous PVDF membrane was arranged in the top layer, it yielded a significantly higher filtrate flux than that with the PCTE membrane on the top layer. The experimental results of the permeability test before and after filtration
(Figure 5.13(b)) show that the ratio of initial permeability and final permeability is still above 85% for the bottom layers. This indicates that external fouling was still dominant during the filtration of protein solutions.

The fouling model accounting for the effects of asymmetric membrane structures was applied to the prediction of the flux decline for both polystyrene microspheres and BSA solutions filtering through the composite membranes. The modeling calculations were based on the parameters listed in Table 5.2 and Table 5.3 for polystyrene microspheres and BSA, respectively. Note that the parameters of normalized permeability ratio $K$ are different for single layer and composite membranes. This is because the composite membranes are thicker than the single layer membranes, thereby they have a larger $K$ as indicated by Eq. (5.9). The compressibility parameter $S_c$ was set to 0.19 and 0.40 for polystyrene microspheres and BSA, respectively. All experimental results were consistent with the model predictions, indicating that a composite membrane with higher pore connectivity in top layer can significantly alleviate the fouling during the filtration.

### 5.5.2.2 Effects of Hydraulic Resistance

In order to validate the model predictions about hydraulic resistance, we formed the pseudo-composite membranes by using two PVDF membranes having the same pore connectivity while varying the pore size of the bottom layer.

First, we filtered 0.00125 g/L polystyrene microsphere solutions through 0.1 $\mu m$ PVDF membrane, and the double-layer membranes with 0.1 $\mu m$ PVDF
membrane in the top layer while the nominal pore size of the bottom layer PVDF membrane was varied from 0.1 to 0.45 µm. Transmembrane pressure was correspondingly varied from 6 to 12 psi to keep the same initial flux of $3 \times 10^{-4}$ m/s. The experimental results were plotted in Figure 5.14(a). It shows that the filtrate flux was increased with increasing hydraulic resistance in the bottom layer (smaller nominal pore size). The results of the permeability test for each layer of the composite membranes were plotted in Figure 5.14(b), and the dominance of external fouling was validated.

The filtration experiments were repeated with 1 g/L BSA solutions as shown in Figure 5.15(a). The initial filtrate flux ranged from $2.9 \times 10^{-4}$ to $3.2 \times 10^{-4}$ m/s. It is demonstrated that the composite membranes with the highest resistance in the bottom layer yielded the lowest flux decline. The corresponding experimental results of the hydraulic permeability test before and after filtration were plotted in Figure 5.15(b). There was no significant internal fouling since the permeability ratio before and after the filtration for the bottom layer was above 85%.

Based on the parameters listed in Table 5.4 (polystyrene microspheres) and Table 5.5 (BSA), the flux decline for the composite membranes with varying resistance on the bottom layer was predicted by the fouling model accounting for the asymmetric membrane structures. The effects of compressibility were included in the modeling calculation for calibrating specific cake layer resistance $R'$ as a function of performance pressure ($S_c = 0.19$ for polystyrene microspheres, $S_c = 0.40$ for BSA). The modeling results were plotted in Figure 5.14(a) and
Figure 5.15(a) as solid curves. The experimental results are consistent with the model prediction, indicating that the composite membrane with higher hydraulic resistance in the bottom layer can reduce the fouling.

5.5.2.3 Comparison of Composite Membranes Based on Productivity and Capacity

In order to compare the performance of composite membranes, we theoretically calculated the volumetric filtrate flux at $2\ h$ after filtering 1 $g/L$ BSA solutions to examine the productivity at this particular time. The system capacity was assumed to be the volume of filtrate per unit membrane area processed until the flux dropped to 10% of the initial value at time $t_c$, and calculated by:

$$\text{Capacity} = \int_0^{t_c} J(t) \, dt$$  \hspace{1cm} (5.22)

All calculations were based on the parameters listed in Table 5.3 and Table 5.5. The calculation results were listed in Table 5.6. It shows that both the instant productivity and capacity of the composite membrane with 0.1 $\mu m$ PVDF membrane on top of 0.1 $\mu m$ PVDF membrane are higher than that for the single layer 0.1 $\mu m$ PVDF membrane. For PCTE and 0.1 $\mu m$ PVDF membranes, the productivity at $2\ h$ is higher for the composite membrane with 0.1 $\mu m$ PVDF membrane on top of 0.2 $\mu m$ PCTE membrane. The system capacity for double-layer 0.1 $\mu m$ PVDF membrane is the highest, which nearly doubled than that for the single layer 0.1 $\mu m$ PVDF membrane. The results indicate that composite membranes can have better productivity and capacity than single-layer membranes.
5.6 Conclusions

A mathematical model accounting for the effects of asymmetric membrane structures on the fouling processes was developed. The permeability ratio describing the pore connectivity and membrane hydraulic resistance was varied in the transverse direction piecewisely to simulate the different asymmetric structures of double-layer composite membranes. The effects of asymmetric structures on the flux decline were theoretically analyzed based on this fouling model. With the plots of normalized pressure profile and the flow streamline, the mechanisms of reducing fouling by asymmetric membrane structures were analyzed. The modeling revealed that the higher pore connectivity in the upper membrane structure was able to allow the fluid to flow into the blocked region, and the higher hydraulic resistance in the lower membrane structure increased the lateral flow.

Based on the fouling parameters and the parameters of membrane morphology, which were determined by filtration experiments of single layer symmetric membranes, the model predictions were compared with the experimental results of double-layer membranes with two membrane combinations: i) 0.2 $\mu$m PCTE membrane on top of 0.1 $\mu$m PVDF membrane and the reversed orientation; ii) 0.1 $\mu$m PVDF membrane on top of different sized PVDF membranes. The model predictions for the flux decline were in good agreement with the experimental results.

All these studies indicate that composite membranes with higher pore
connectivity in the upper layer and higher hydraulic resistance in the lower layer are better than the others providing that the dominant fouling mechanism is external fouling. This optimized morphology has the potential to help to design new membranes with better fouling resistance.
Table 5.1 Best Fit Parameters From 0.2 µm PCTE Membrane

<table>
<thead>
<tr>
<th>Solutions</th>
<th>$\alpha$ ($m^2/kg$)</th>
<th>$fR'$ ($m/kg$)</th>
<th>$R_{c0}$ ($m^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>0.25 µm PS Bead</td>
<td>$1.6 \pm 0.1 \times 10^4$</td>
<td>$3.8 \pm 0.1 \times 10^{13}$</td>
<td>$1.8 \pm 0.2 \times 10^{10}$</td>
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<tr>
<td>BSA</td>
<td>$6.3 \pm 0.2$</td>
<td>$4.2 \pm 0.1 \times 10^{11}$</td>
<td>$1.6 \pm 0.3 \times 10^{10}$</td>
</tr>
<tr>
<td>Parameter</td>
<td>0.2 μm PCTE</td>
<td>0.1 μm PVDF</td>
<td>0.2 μm PCTE</td>
</tr>
<tr>
<td>-----------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>( \alpha' ) (m²/kg)</td>
<td>5.7×10³</td>
<td>5.7×10³</td>
<td>5.7×10³</td>
</tr>
<tr>
<td>( f'R' ) (m/kg)</td>
<td>3.8×10¹³</td>
<td>4.7×10¹³</td>
<td>4.9×10¹³</td>
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<td>( R_{c0} ) (m⁻¹)</td>
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<td>1.8×10¹⁰</td>
<td>1.8×10¹⁰</td>
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<tr>
<td>( K_{top} )</td>
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<td>0</td>
</tr>
<tr>
<td>( K_{bottom} )</td>
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Table 5.3 Parameters of Model Calculations for BSA + Membrane Combination I

<table>
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<tr>
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<th>0.2 μm PCTE</th>
<th>0.1 μm PVDF</th>
<th>0.2 μm PCTE / 0.1 μm PVDF</th>
<th>0.1 μm PVDF</th>
<th>0.2 μm PCTE / 0.1 μm PVDF</th>
</tr>
</thead>
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<tr>
<td>$\alpha'$ (m²/kg)</td>
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<td>$f'K'$ (m/kg)</td>
<td>$4.2 \times 10^{13}$</td>
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<td>$K_{bottom}$</td>
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Table 5.4 Parameters of Model Calculations for PS Bead + Membrane Combination II

<table>
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<th>0.1 µm PVDF</th>
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<th>0.1 µm PVDF</th>
<th>0.1 µm PVDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha' )  (m²/kg)</td>
<td>5.7×10³</td>
<td>5.7×10³</td>
<td>5.7×10³</td>
<td>5.7×10³</td>
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<tr>
<td>( f R' )  (m/kg)</td>
<td>4.7×10¹³</td>
<td>4.7×10¹³</td>
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<tr>
<td>( R_{e0} )  (m⁻¹)</td>
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<td>( K_{top} )</td>
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<td>( K_{bottom} )</td>
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Table 5.5 Parameters of Model Calculations for BSA + Membrane Combination II

<table>
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<tr>
<th>Parameter</th>
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<th>0.1 μm PVDF / 0.45 μm PVDF</th>
<th>0.1 μm PVDF / 0.22 μm PVDF</th>
<th>0.1 μm PVDF / 0.1 μm PVDF</th>
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<tbody>
<tr>
<td>$\alpha'$ (m²/kg)</td>
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<td>1.4</td>
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<tr>
<td>$fK'$ (m/kg)</td>
<td>6.5x10^{13}</td>
<td>6.5x10^{13}</td>
<td>7.3x10^{13}</td>
<td>8.6x10^{13}</td>
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<tr>
<td>$R_{c0}$ (m⁻¹)</td>
<td>5.1x10^{10}</td>
<td>5.1x10^{10}</td>
<td>5.1x10^{10}</td>
<td>5.1x10^{10}</td>
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<tr>
<td>$K_{top}$</td>
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<td>3.44</td>
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<td>$K_{bottom}$</td>
<td>3.44</td>
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### Table 5.6 Instant Productivity and Capacity for BSA Solution (1g/L)

<table>
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<tr>
<th>Membrane Combination</th>
<th>Instant Productivity after 2 h ((\times10^{-8} \text{ m}^3/\text{s}))</th>
<th>Capacity ((\text{m}^3/\text{m}^2))</th>
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<tbody>
<tr>
<td>0.2 (\mu\text{m}) PCTE</td>
<td>2.65</td>
<td>2.61</td>
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<tr>
<td>0.1 (\mu\text{m}) PVDF</td>
<td>6.98</td>
<td>16.90</td>
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<td>0.2 (\mu\text{m}) PCTE / 0.1 (\mu\text{m}) PVDF</td>
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<td>6.66</td>
</tr>
<tr>
<td>0.1 (\mu\text{m}) PVDF / 0.2 (\mu\text{m}) PCTE</td>
<td>7.84</td>
<td>21.55</td>
</tr>
<tr>
<td>0.1 (\mu\text{m}) PVDF / 0.45 (\mu\text{m}) PVDF</td>
<td>7.10</td>
<td>17.88</td>
</tr>
<tr>
<td>0.1 (\mu\text{m}) PVDF / 0.22 (\mu\text{m}) PVDF</td>
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<td>22.11</td>
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<tr>
<td>0.1 (\mu\text{m}) PVDF / 0.1 (\mu\text{m}) PVDF</td>
<td>8.66</td>
<td>32.76</td>
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</table>
Figure 5.1 The effects of hydraulic resistance $R_m$ and pore connectivity $K$ of an asymmetric composite membrane on normalized flow rate when the cake layer is impermeable ($\theta=0.64$): a) $K_{\text{bottom}}$ is constant b) $K_{\text{top}}$ is constant.
Figure 5.2 The effects of hydraulic resistance $R_m$ and pore connectivity $K$ of an asymmetric composite membrane on normalized flow rate when the cake layer is permeable ($\theta=0.64$): a) $K_{\text{bottom}}$ is constant b) $K_{\text{top}}$ is constant.
Figure 5.3 Normalized flow rate as a function of the fraction of impermeable blocked area for asymmetric composite membranes when varying $k_r$. 

<table>
<thead>
<tr>
<th>$k_{z\text{bottom}}/k_{z\text{top}}$</th>
<th>$k_{r\text{top}}/k_{z\text{top}}$</th>
<th>$k_{z\text{bottom}}/k_{z\text{bottom}}$</th>
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Figure 5.1(a2)
Figure 5.4 The effects of varying $k_r$ on a) normalized pressure profiles and b) flow streamlines of the asymmetric composite membranes ($\theta=0.64$).
Figure 5.5 Normalized flow rate as a function of the fraction of impermeable blocked area for asymmetric composite membranes when varying $k_z$. 

Figure 5.1(a2) 

<table>
<thead>
<tr>
<th>$k_{z\text{bottom}}/k_{z\text{top}}$</th>
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<th>$k_{\text{rbottom}}/k_{z\text{bottom}}$</th>
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<td>100</td>
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Figure 5.6 The effects of varying $k_z$ on a) normalized pressure profiles and b) flow streamlines of the asymmetric composite membranes ($\theta = 0.64$).
Figure 5.7 Normalized flow rate as a function of the fraction of impermeable blocked area for asymmetric composite membranes when varying both $k_r$ and $k_z$. 

![Diagram showing normalized flow rate as a function of fraction of blocked area with different lines representing varying $k_r/k_z$ ratios.](image)
Figure 5.8 The effects of varying both $k_r$ and $k_z$ on a) normalized pressure profiles and b) flow streamlines of the asymmetric composite membranes ($\theta=0.64$).
Figure 5.9 0.25µm PS beads filtered through a) 0.1µm PCTE membrane (straight-through pores) and b) 0.1µm PVDF membrane (highly interconnected pores). The solid curves are the model calculations based on the fouling model accounting for the membrane morphology.
Figure 5.10 BSA filtered through a) 0.1 µm PCTE membrane (straight-through pores) and b) 0.1 µm PVDF membrane (highly interconnected pores). The solid curves are the model calculations based on the fouling model accounting for the membrane morphology.
Figure 5.11 Experimental data fitting of compressibility parameter $S_c$ for a) PS beads and b) BSA

\[
\ln(R_{\text{total}} - R_m - R_c) = S_c \cdot \ln\left(\frac{\Delta p}{1N/m^2}\right) + \ln(k_m)
\]

PS Beads $S_c = 0.21 \pm 0.03$

BSA $S_c = 0.37 \pm 0.04$
Figure 5.12 0.25 μm PS beads filtered through the composite membranes with 0.2 μm PCTE on the top of 0.1 μm PVDF or the reversed orientation: a) flux decline data (solid curves are model calculations based on the parameters in Table 5.2) b) the ratio of permeability before and after filtration.
Figure 5.13 BSA filtered through the composite membranes with 0.2 μm PCTE on the top of 0.1 μm PVDF or the reversed orientation: a) flux decline data (solid curves are model calculations based on the parameters in Table 5.3) b) the ratio of permeability before and after filtration.
Figure 5.14 0.25 µm PS beads filtered through the composite membranes with 0.1 µm PVDF on the top of different sized PVDF: a) flux decline data (solid curves are model calculations based on the parameters in Table 5.4) b) the ratio of permeability before and after filtration.
Figure 5.15 BSA filtered through the composite membranes with 0.1 µm PVDF on the top of different sized PVDF: a) flux decline data (solid curves are model calculations based on the parameters in Table 5.5) b) the ratio of permeability before and after filtration.
CHAPTER 6  A-Priori Estimation for Fouling Parameters in the Combined Pore Blockage and Cake Filtration Model

6.1 Introduction

As shown in section 1.3.1, Most of fouling models with continuum approaches employed some differential relationships, e.g., Eqs. (1.5), (1.9), and (1.13), to depict the fouling rates of different fouling mechanisms. These mathematical models involve the parameters which have physical meaning. However, these fouling parameters were previously obtained by fitting mathematical models with experimental flux decline data [75, 124, 153, 155, 241].

Ho and Zydney [75] developed a combined fouling model accounting for both pore blockage and cake filtration. In this model (section 1.3.1.2), the membrane surface is gradually covered by foulants, and an inhomogeneous cake layer is formed within the blocked area. There are three critical fouling parameters in the mathematical expression for this model (Eq. (1.26)): pore blockage parameter $\alpha$, specific cake layer resistance $R'$, and the initial resistance single particle $R_{c0}$. All of them have physical meaning, which indicate the relationships between fouling rate and the properties of both feed and membrane.

Silalahi et al. [242] showed that both 2D and 3D visualization techniques were
able to clarify the fouling mechanism as the effect of different particle sizes. Khan et al. [243] found that the membrane fouling in a membrane bioreactor (MBR) can be significantly mitigated by appropriate shear stress on the membrane fibers, which could reduce the mean particle size. Ivanovic et al. [244] redesigned the submerged hollow fiber membrane reactor by introducing a flocculation zone in the membrane module, which could prevent submicron particles from contacting the membrane surface for better fouling control. Park et al. [245] experimentally studied the effects of cake layer structure on the fouling in reverse osmosis membranes, and demonstrated that the rate of flux decline decreased significantly with an increase of the ionic strength as well as particle size. Meng et al. [246] characterized the cake layer in a submerged membrane bioreactor with various modern techniques, and found that the fouling was mainly attributed to the small particles in sludge suspension. Lee et al. [247] summarized the methods for determining the porosity of a bio-cake in a MBR, and correlated the bio-cake architecture with the membrane filterability. Ho and Zydney [128] found that the rate of pore blockage during microfiltration can be affected by the membrane surface porosity. All these studies revealed the impacts of feed characteristics and membrane properties on fouling processes.

The industrial applications of microfiltration usually involve multi-component feeds, which have the potential to cause severe membrane fouling. One typical process is the purification of proteins from a fermentation broth containing yeast cells [248, 249]. Several studies [42, 43, 69, 250-252] experimentally investigated the
fouling processes with the multi-component feeds, and found that the larger components such as microorganisms are typically rejected at the membrane surface to form a cake layer, which may behave as a dynamic membrane to prevent the smaller foulants from reaching the membrane surface. However, the principles behind these fouling processes remained unknown.

The objective of this study was to provide an a-priori estimation for the primary fouling parameters in the combined pore blockage and cake filtration fouling model developed by Ho and Zydney [75]. These fouling parameters were mathematically correlated with the feed characteristics and membrane properties. The sensitivity of these parameters was theoretically investigated. Then, the model predictions based on the estimated fouling parameters were validated by a variety of feed solutions, including polystyrene microspheres, proteins, and binary mixtures containing both polystyrene microspheres and proteins.

6.2 Model Development

In order to account for the effects of foulant shape on the fouling parameters, we characterized foulant particles as oblate spheroids with different sphericity. Sphericity is defined as the ratio of the surface area of a sphere with the same volume as the particle, to the surface of the particle [253]. As schematically shown in Figure 6.1, the oblate spheroid has two equal equatorial radii \( r_{pa} = r_{pb} \), and a polar radius \( r_{pc} \leq r_{pa} \). The sphericity of the oblate spheroid can be calculated by:
\[ \Phi_s = \frac{2\left(\frac{r_{pa}^2 r_{pc}}{r_{pa}}\right)^2}{\arctan h\left[\sin\left(\arccos\frac{r_{pc}}{r_{pa}}\right)\right]} \]

(6.1)

Obviously, \( \Phi_s \) is equal to 1 for perfect spheroid, and less than 1 when \( r_{pc} \) is shorter than \( r_{pa} \). The volume equivalent particle radius is defined as:

\[ r_p = \left(\frac{r_{pa}^2 r_{pc}}{r_{pa}}\right)^{\frac{1}{3}} \]

(6.2)

Since we are focused on the external fouling, here, \( C'_b \) is defined as the concentration of the foulant, which has a relatively large size compared to the pore size on the membrane surface. If \( f' \) is the mass fraction of the foulant in the feed solution, the relationship between the concentration of the feed solution \( C_b \) and the concentration of the foulant \( C'_b \) can be given by:

\[ C'_b = f'C_b \]

(6.3)

### 6.2.1 Fouling Parameters for Pore Blockage

For pore blockage, the fouling parameter \( \alpha \) is defined as the blocked membrane area per unit mass of foulant particles. Based on this definition, we can mathematically relate \( \alpha \) to particle shape \( r_p \), particle density \( \rho_p \), membrane pore size \( r_m \), and membrane surface porosity \( \varepsilon_{ms} \) by:

\[ \alpha = \frac{\text{blocked membrane area}}{\text{particle mass}} = n_s \frac{3r_m^2}{\varepsilon_{ms} r_p^3 \rho_p} \]

(6.4)

where \( n_s \) is the number of membrane surface pores covered by one foulant particle.
In this study, we assume that $n_s$ is an integer, and can be roughly estimated by:

\[
    n_s = \begin{cases} 
        1 & \text{at } \pi r_{pa}^2 \leq \pi \frac{r_m^2}{\varepsilon_{ms}} \\
        \text{round} \left( \frac{r_{pa}^2}{r_m^2 \varepsilon_{ms}} \right) & \text{at } \pi r_{pa}^2 > \pi \frac{r_m^2}{\varepsilon_{ms}}
    \end{cases}
\]  

(6.5)

Note that $n_s$ is estimated by $r_{pa}$ other than $r_p$. This is because we implicitly assume that the foulant particles always cover the membrane pores with the maximum projected area.

When the feed solution contains different sized foulant particles, the total rate of blocked membrane area change is a linear combination of the contributions by each particle:

\[
    \frac{dA_c}{dt} = Q_u C'_b \sum_i \alpha_i \frac{C'_i}{C'_b}
\]

(6.6)

If $\omega_i$ is defined as the mass fraction of foulant particle $i$, we can obtain $\alpha$ for the mixture as:

\[
    \alpha = \sum_i \omega_i \alpha_i
\]

(6.7)

### 6.2.2 Fouling Parameters for Cake Filtration

The critical problem for cake filtration is how to estimate the rate of cake layer resistance change, which is characterized by the specific resistance of the cake layer $R'$ in the combined fouling model [75]. As summarized by Endo et al. [254], there are two primary ways to estimate the permeation of the particle packed layer, i.e., channel theory (internal flow model, an approach similar to that used for the
Kozeny-Carman equation [161]) and drag theory (external flow model, an approach similar to that used for the Burke-Plummer equation [255]).

In the current study, we employed the channel theory to derive the permeation equations for the cake layer on the membrane surface. Therefore, the basic assumptions for deriving the Kozeny-Carman equation were included in our new mathematical models: i) particle layer is uniform; ii) voids in the particle layer consist of a bundle of tortuous channels with length of \( L_e \) and noncircular cross-section; iii) pressure drop can be described by the Hagen-Poiseuille equation:

\[
\Delta p_e = \frac{32 \mu u_c}{D_e^2} L_e
\]  

(6.8)

where \( \Delta p_e \) is the total pressure drop through the cake layer, \( u_c \) is the fluid velocity within the cake layer channel, and \( D_e \) is the imaginary diameter of the cake layer channel. The actual velocity \( u_c \) can be converted to the average flux based on the total membrane area by [256]:

\[
J = u_c \epsilon_c \frac{L_c}{L_e}
\]  

(6.9)

For a noncircular channel, the imaginary diameter \( D_e \) is four times the hydraulic radius:

\[
D_e = 4 \frac{\text{volume of cake layer voids}}{\text{surface area of particles}} = 4 \frac{\epsilon_c}{1 - \epsilon_c} \frac{1}{S_v}
\]  

(6.10)

where \( S_v \) is the specific particle surface area based on particle volume. It is a function of particle shape, particle size, and particle size distribution. The definition
for the hydraulic radius was mainly used for calculations involving turbulent flow, which could force the fluid into the corners of the channels. Here, for simplicity, we neglected the effects of the secondary flow, and employed this relationship for the porous cake layer. The derived equations for $S_v$ taking into account the particle polydispersity were listed in Table 6.1.

Combining Eqs. (6.8), (6.9), and (6.10), we can obtain the mathematical equation for the cake layer resistance:

$$R_c = \frac{2\tau^2 (1-\epsilon_c)^2 S_v^2}{\epsilon_c^4} L_c$$

(6.11)

where $L_c$ is the thickness of the cake layer, and $\tau$ is the tortuosity of the cake layer as defined by:

$$\tau = \frac{L_c}{L_c}$$

(6.12)

The relationship for $\tau$ versus $\epsilon_c$ for dense granular packings can be given by a power law [257]:

$$\tau = \frac{1}{\epsilon_c^{0.5}}$$

(6.13)

Substituting Eq. (6.13) into the differentiated Eq. (6.11), we can obtain the rate of cake layer resistance change:

$$\frac{dR_c}{dt} = \frac{2(1-\epsilon_c)^2 S_v^2}{\epsilon_c^4} \frac{dL_c}{dt}$$

(6.14)

When we take the particle polydispersity into account, the rate of cake layer thickness
change can be given by:

$$\frac{dL_c}{dt} = \frac{J_b}{1 - \varepsilon_c} \sum_i \frac{C_{bi}'}{\rho_{pi}}$$  \hspace{1cm} (6.15)$$

Combining Eqs. (6.14) and (6.15), we can get:

$$\frac{dR_c}{dt} = \frac{2(1 - \varepsilon_c)^2}{\varepsilon_c' \bar{\rho}_p} S_v^2 C_b' J_b$$  \hspace{1cm} (6.16)$$

where $\bar{\rho}_p$ is the mass weighted average particle density defined as:

$$\bar{\rho}_p = \left( \sum_i \frac{\omega_i}{\rho_{pi}} \right)^{-1}$$  \hspace{1cm} (6.17)$$

Comparing Eq. (6.16) with the cake filtration model (Eq. (4.10)), Finally, we get the mathematical equation for specific resistance of the cake layer:

$$R' = \frac{2(1 - \varepsilon_c)}{\varepsilon_c' \bar{\rho}_p} S_v^2$$  \hspace{1cm} (6.18)$$

6.3 Experimental Methods

6.3.1 Experimental Materials

Polystyrene microspheres with different sizes, including 0.25$\mu$m, 0.46$\mu$m, and 0.54$\mu$m were employed to experimentally study the effects of particle size on the fouling parameters. The protein solutions used in this study include BSA and $\alpha$-casein solutions. We also prepared binary mixtures containing both polystyrene microspheres and proteins by carefully dissolving the weighted protein powder (BSA
or α-casein) into the prepared polystyrene microsphere solutions. The detailed information about polystyrene microspheres and proteins used in the current studies was introduced in section 3.2.

Both the 0.2 μm PCTE membrane (GTTP) and 0.2 μm aluminum oxide membrane (Anopore) were used for flux decline measurements. Both membranes have the uniform straight-through cylindrical pores. 0.2 μm Anopore membranes have a larger porosity (ε = 0.6) compared to 0.2 μm PCTE membrane (ε ranges from 0.05 to 0.20). The detailed information about these two membranes was listed in Table 3.2.

6.3.2 Feed Characterization

The particle size and particle size distribution of the protein solutions were determined by the dynamic light scattering (DLS) measurements as introduced in section 3.3.2.2. The concentration of the protein solutions were 2 g/L and 0.001 g/L for BSA and α-casein, respectively.

In order to measure the mass fraction of the foulant particles in the protein solutions (f′), we fouled the 0.2 μm PCTE membranes with the protein solutions (4 g/L for BSA, 0.004 g/L for α-casein) at a transmembrane pressure of 4 psi. The mass of the clean membrane m_{clean} was measured before the filtration. When the total volume of the filtrate was larger than 500 mL, the exact filtrate volume was recorded. At the same time, the feed solution was replaced by DI water to flush the fouled membrane for at least 0.5 h. The fouled membrane was directly air-dried at
4°C, and then, the completely dried membrane was weighed \((m_{\text{fouled}})\) by a digital balance (AG204, DeltaRange, Mettler Toledo) with 0.0001 accuracy. The mass fraction of the foulant (particle size is larger than 0.2 \(\mu m\)) in the protein solutions can be calculated by:

\[
f' = \frac{m_{\text{fouled}} - m_{\text{clean}}}{C_b V}
\]  

(6.19)

The porosity of the cake layer \(\varepsilon_c\) and the initial resistance of the single foulant particle were determined by linearly fitting the experimental data of \(R_{\text{total}} - R_m\) versus \(V\). The 0.2 \(\mu m\) PCTE or 0.2 \(\mu m\) Anopore membranes were first fouled by the solutions, including different sized polystyrene microspheres (0.001 \(g/L\)), BSA (1 \(g/L\)), and \(\alpha\)-casein (0.001 \(g/L\)), for at least 100 \(mL\) so that a relatively uniform cake layer could be formed on the membrane surface. Then, the total membrane resistance \((R_{\text{total}} = \frac{\Delta p}{\mu J})\) was measured as a function of the total filtrate volume \(V\) at a transmembrane pressure of 2 psi. In terms of Eq. (6.11), the linear relationship between \(R_c\) and \(V\) can be given by:

\[
R_c = \frac{2(1-\varepsilon_c)^2}{\varepsilon_c^4 P^2 \rho S_v^2 C_b V}
\]  

(6.20)

Therefore, \(\varepsilon_c\) can be calculated from the slope of trendline based on the experimental data \(R_{\text{total}} - R_m\) versus \(V\). \(R_{c0}\) can be obtained from the intercept of trendline of \(R_{\text{total}} - R_m\) versus \(V\).

Scanning electron microscopy (SEM) was also used to characterize the cake layer formed on the membrane surface. The cake layer samples were prepared by
fouling 0.22 \( \mu m \) PVDF membranes with 0.46 \( \mu m \) polystyrene microspheres (0.002 g/L, 1 L, 2 psi), and BSA (2 g/L, 2 h, 2 psi). Instead of PCTE membranes, we prepared the cake layer samples with PVDF membranes due to the fact that it is easier to fracture the PVDF membrane so that we could get a better cross-section of the cake layer. We also fouled the 0.2 \( \mu m \) PCTE membrane with a binary mixture containing both 0.25 \( \mu m \) polystyrene microspheres (0.001 g/L) and BSA (1 g/L) to prepare the sample for observing the surface of the cake layer formed by a complex mixture. The detailed procedures for SEM measurements were introduced in section 3.3.2.1.

6.3.3 Filtration Experiment

The common performance of the filtration experiment is introduced in section 3.3.1. The transmembrane pressure \( \Delta p \) applied in this work was 2 psi for filtration experiments with 0.2 \( \mu m \) PCTE membranes or 2.5 psi for filtration experiments with 0.2 \( \mu m \) Anopore membranes.

The concentration of polystyrene microsphere solutions, including 0.25 \( \mu m \), 0.46 \( \mu m \), and 0.54 \( \mu m \) polystyrene microspheres, was varied from 0.000625 to 0.005 g/L. The polystyrene microsphere solutions were filtered through both 0.2 \( \mu m \) PCTE and 0.2 \( \mu m \) Anopore membranes. A BSA solution with concentration varying from 1 to 8 g/L and an \( \alpha \)-casein solution with concentration varying from 0.0005 to 0.004 g/L were filtered through 0.2 \( \mu m \) PCTE membranes.
The binary mixtures, including 0.25 μm polystyrene microspheres mixed with 0.54 μm polystyrene microspheres, 0.25 μm polystyrene microspheres mixed with BSA, and 0.25 μm polystyrene microspheres mixed with α-casein, were filtered through 0.2 μm PCTE membranes. The total concentration of the foulant particles with size larger than the membrane pore size, was fixed at 0.00125 g/L for all binary mixtures. The mass fraction of the 0.25 μm polystyrene microspheres (based on the total foulant mass in the solutions) was varied from 0 to 1.

6.4 Results and Discussion

6.4.1 Parameter Sensitivity Analysis

As derived in section 6.2, the external fouling parameters were correlated with a variety of parameters including: feed characteristics ($r_p$, $r_{pc}$, $ρ_p$, and $ε_c$), and membrane properties ($r_m$, $ε_m$). Roughly, we can refer to these parameters as independent variables in the mathematical fouling model (this may not be true for $ε_c$ when the particle is nonspherical). In addition, the mathematical fouling model accounting for both pore blockage and cake filtration also involves some parameters dealing with the interaction between the membrane and foulant particles, e.g., $n_s$ indicating the size ratio of foulant particle to membrane pore, and $R_{c0}$ indicating the adhesion force between foulant particle and membrane surface. The variations of these parameters may have significant impact on the model predictions. Therefore,
the partial derivative-based sensitivity analysis [258] was employed to provide a deeper insight into the interplay between these parameters and model predictions.

6.4.1.1 Feed Characteristics

First, the effects of particle size was studied by calculating the partial derivative of the normalized flow rate with respect to $r_p$ as varying both particle size $\Phi$ from 0.25 to 0.5 $\mu m$ and filtration time from 0 to 120 min. The other parameters were fixed ($\Delta p = 2$ psi, $C_b = 0.0005$ $g/L$, $\rho_p = 1.05 \times 10^3$ $kg/m^3$, $\Phi_s = 1$, $\epsilon_c = 0.25$, $\epsilon_{ms} = 0.15$, $R_m = 5 \times 10^{10}$ $m^{-1}$, and $R_e0 = 2 \times 10^{10}$ $m^{-1}$). The calculation results were plotted in Figure 6.2(a). The regions with deeper grayscale have the relatively higher sensitivity of $r_p$ compared to the others. We also plotted the contours of $t_\alpha$ (characteristic time of pore blockage as defined in Table 4.3) and $t_\gamma$ (characteristic time of cake filtration as defined in Table 4.3) in Figure 6.2(a). It shows that the sensitivity is reduced with increasing particle size. In the positive direction of filtration time axis, there are two regions with locally high sensitivity around $t_\alpha$ and $t_\gamma$. The region around $t_\alpha$ has higher sensitivity than that around $t_\gamma$. This is consistent with the fact that both $\alpha$ and $R'$ are related to $r_p$ as shown in Eqs. (6.4) and (6.18).

In Figure 6.2(b), the partial derivatives of normalized flow rate with respect to the particle aspect ratio ($\frac{r_{pc}}{r_{pa}}$) were plotted as functions of both particle aspect ratio and filtration time. The particle aspect ratio indicates the particle shape in our model.
\( \frac{r_{pc}}{r_{pa}} = 1 \) for a perfect spheroid, \( \frac{r_{pc}}{r_{pa}} < 1 \) for an oblate spheroid), and its value was varied from 0.2 to 1 while keeping the other parameters at \( \Delta p = 2 \text{ psi} \), \( C_b = 0.0005 \text{ g}/L \), \( \rho_p = 1.05 \times 10^3 \text{ kg}/m^3 \), \( r_p = 0.25 \mu m \), \( \varepsilon_c = 0.25 \), \( \varepsilon_{ms} = 0.15 \), \( R_m = 5 \times 10^{10} \text{ m}^{-1} \), and \( R_{c0} = 2 \times 10^{10} \text{ m}^{-1} \). It shows that reducing the particle aspect ratio significantly increases the sensitivity when the particle aspect ratio is less than 0.3. We also note that most of the regions with high sensitivity are beyond the contour of \( t_\gamma \). Although the value of \( \frac{r_{pc}}{r_{pa}} \) can affect \( n_s \), which was included in the equation (6.4) for \( \alpha \), the value of \( r_p \) (0.25 \( \mu m \)) used in this test is relatively small compared to the membrane pore size (0.2 \( \mu m \)) so that \( n_s \) is essentially fixed at 1. Hence, the effects of \( \frac{r_{pc}}{r_{pa}} \) on \( n_s \), thereby on \( \alpha \), are technically neglected. We will discuss how \( n_s \) affect the flux decline in a later section.

The effects of particle density on the normalized flow rate were shown in Figure 6.2(c). The value of \( \rho_p \) ranges from \( 1 \times 10^3 \) to \( 2 \times 10^3 \text{ kg}/m^3 \) while the other parameters are fixed at \( \Delta p = 2 \text{ psi} \), \( C_b = 0.0005 \text{ g}/L \), \( \Phi_S = 1 \), \( r_p = 0.25 \mu m \), \( \varepsilon_c = 0.25 \), \( \varepsilon_{ms} = 0.15 \), \( R_m = 5 \times 10^{10} \text{ m}^{-1} \), and \( R_{c0} = 2 \times 10^{10} \text{ m}^{-1} \). It shows that increasing \( \rho_p \) decreases the sensitivity. The regions around the contours of both \( t_\alpha \) and \( t_\beta \) have higher sensitivity than the other regions. This is because both \( \alpha \) and \( R' \) are defined based on the unit mass of foulant particles yielding the term of \( \rho_p \) in the denominator of mathematical equations for both \( \alpha \) and \( R' \).

Cake layer porosity is directly related to the resistance of the cake layer. As a
result, in Figure 6.2(d), we can see that the regions of high sensitivity are all beyond the contours of $t_γ$. We also note that the normalized flow rate is more sensitive to the low cake layer porosity.

In conclusion, all discussed parameters for feed characteristics ($r_p$, $r_{pc}$, $r_{pa}$, $ρ_p$, and $ε_ε$) have positive impacts on the normalized flow rate. The regions of high sensitivity can be correlated with the characteristic times for pore blockage and cake filtration.

### 6.4.1.2 Membrane Properties

Since we were focused on the external fouling in the current studies, only membrane pore size $r_m$ (for straight-through cylindrical pores), and membrane surface porosity $ε_{ms}$ were discussed in analyzing how the membrane properties affect the normalized flow rate based on the combined fouling model accounting for both pore blockage and cake filtration.

Figure 6.3(a) shows the absolute value of the derivative of normalized flow rate with respect to $r_m$ in that the pore blockage rate is increased by increasing membrane pore size. Here, the value of $n_s$ was implicitly fixed at 1 as the membrane pore size was varied from 0.1 to 0.2 $\mu$m while keeping the particle size at 0.25 $\mu$m and membrane surface porosity at 0.15. The other fixed parameters were $Δp = 2$ psi, $C_b = 0.0005 \text{ g/L}$, $Φ_s = 1$, $ρ_p = 1.05 × 10^3 \text{ kg/m}^3$, $ε_ε = 0.25$, $R_m = 5 × 10^{10} \text{ m}^{-1}$, and $R_{ε0} = 2 × 10^{10} \text{ m}^{-1}$. It shows that the tested range of membrane pore size does not have a significant impact on the sensitivity, and the high sensitivity
regions are concentrated within the initial filtration, and earlier than $t_\alpha$.

The membrane surface porosity is implicitly related to the pore density (number of pores per unit membrane area). When the membrane pore size is fixed, decreasing $\varepsilon_{ms}$ yields lower pore density, thereby larger blocked area. The calculation results of the partial derivative of normalized flow rate with respect to $\varepsilon_{ms}$ were plotted in Figure 6.3(c) ($\Delta p = 2$ psi, $C_b = 0.0005$ g/L, $\Phi_s = 1$, $\rho_p = 1.05 \times 10^3$ kg/m$^3$, $\mu = 0.2$ $\mu$m, $R_m = 5 \times 10^{10}$ m$^{-1}$, and $R_{c0} = 2 \times 10^{10}$ m$^{-1}$). It shows that the normalized flow rate is more sensitive to $\varepsilon_{ms}$ with lower values ($\leq 0.2$). It also clearly demonstrates that the regions with high sensitivity to $\varepsilon_{ms}$ are constrained around the contour of $t_\alpha$.

Obviously, only the rate of pore blockage is affected by both $r_m$ and $\varepsilon_{ms}$. $\varepsilon_{ms}$ has positive impact on the normalized flow rate, while $r_m$ has negative impact on the normalized flow rate. The regions of high sensitivity to $r_m$ or $\varepsilon_{ms}$ have strong correlations with the characteristic time for pore blockage.

6.4.1.3 Interaction between Membrane and Foulants

$n_s$ and $R_{c0}$ are actually lumped parameters indicating the interaction between membrane and foulant particles. As shown by Eq. (6.5), $n_s$ is mathematically related to particle size, membrane pore size, and membrane surface porosity. However, the mathematical model for predicting $R_{c0}$ is still unclear in the current studies. Therefore, we roughly refer to $R_{c0}$ as an independent variable in the partial derivative-based sensitivity analysis.
As shown in Figure 6.4(a) for the partial derivative of normalized flow rate with respect to $n_t$, the value of $n_t$ was varied from 1 to 25 ($\Delta p = 2 \text{ psi}$, $C_b = 0.0005 \text{ g/L}$, $\Phi_x = 1$, $\rho_p = 1.05 \times 10^3 \text{ kg/m}^3$, $\varepsilon_c = 0.25$, $r_m = 0.2 \mu m$, $\varepsilon_m = 0.15$, $R_m = 5 \times 10^{10} \text{ m}^{-1}$, and $R_{c_0} = 2 \times 10^{10} \text{ m}^{-1}$). Here, we implicitly assumed that the variation of $n_t$ was caused by the change of particle size ($r_p = \sqrt{\frac{n_x r_m^2}{\varepsilon_m}}$). It shows that the normalized flow rate is more sensitive to $n_t$ when $n_t$ has a relatively low value. Although the regions of high sensitivity to $n_t$ are concentrated at long filtration times, it does not show a strong correlation between the sensitive regions and the contour of characteristic time.

The effects of $R_{c_0}$ were studied by calculating the partial derivative of normalized flow rate with respect to $\frac{R_{c_0}}{R_m}$. As shown in Figure 6.4(b), the value of $\frac{R_{c_0}}{R_m}$ was varied from 0.1 to 2 while fixing the parameters at $\Delta p = 2 \text{ psi}$, $C_b = 0.0005 \text{ g/L}$, $r_p = 0.25 \mu m$, $\Phi_x = 1$, $\rho_p = 1.05 \times 10^3 \text{ kg/m}^3$, $\varepsilon_c = 0.25$, $r_m = 0.2 \mu m$, $\varepsilon_m = 0.15$, and $R_m = 5 \times 10^{10} \text{ m}^{-1}$. It shows that increasing $\frac{R_{c_0}}{R_m}$ yields a higher normalized flow rate (negative derivative), and increases the extent of sensitivity. The region of high sensitivity to $\frac{R_{c_0}}{R_m}$ is at the initial filtration time with a weak correlation to the characteristic time for pore blockage $t_\alpha$.

### 6.4.2 Model Validation with Single Component Solutions

In this section, the estimation of the external fouling parameters was validated
with single component solutions, including different sized polystyrene microspheres and protein solutions. First, we determined the parameters for the feed characteristics with independent experiments. Then, we calculated the external fouling parameters based on the equations derived in section 6.2, and compared the modeling predictions with the results of filtration experiments.

6.4.2.1 Polystyrene Microspheres

As introduced in section 3.2.2, polystyrene microspheres have uniform size and nearly perfect shape ($\Phi_s = 1$). The particle density of all different sized polystyrene microspheres is $1.05 \times 10^3 \text{kg/m}^3$. The specific volume based on the particle surface area $V_s$ was calculated based on the equation for a perfect spheroid as listed in Table 6.1.

We experimentally determined the porosity of the polystyrene microsphere cake layer and the initial resistance of a single foulant particle $R_{c0}$ based on both 0.2 $\mu$m PCTE and Anopore membranes following the procedures in section 6.3.2. The experimental results were plotted in Figure 6.5 (a) for 0.2 $\mu$m PCTE membrane and (b) for 0.2 $\mu$m Anopore membrane.

Based on the trendline slope of the experimental data of $R_{\text{total}} - R_m$ versus $V$, the cake layer porosity $\varepsilon_c$ of the polystyrene microspheres was calculated as 0.34 with an error less than 0.02 (Eq. (6.20)). This value is close to the value reported in earlier studies [259, 260] for random close packing ($\varepsilon_c = 0.36$), which was determined by computer simulation. This is also consistent with the SEM images as
shown in Figure 6.6. The total filtrate volume was 600 mL yielding a cake layer with a thickness of 4.6±0.1 µm as shown in Figure 6.6(b). Then, \( \varepsilon_c \) was estimated based on the equation:

\[
\varepsilon_c = 1 - \frac{C_b V}{\rho L_c A_m}
\]  

(6.21)

The calculated \( \varepsilon_c \) based on the SEM images is 0.363, which is almost equal to the reported value based on computer simulation.

\( R_{c,0} \) for polystyrene microspheres based on 0.2 µm PCTE and Anopore membranes was obtained from the value of the trendline intercept in the plots of \( R_{total} - R_m \) versus \( V \) (Figure 6.5). The value of \( R_{c,0} \) based on the 0.2 µm PCTE membrane for different sized polystyrene microspheres ranges from 1.8×10\(^{10} \) to 1.5×10\(^{10} \) m\(^{-1} \). Although the value for particles with a larger size is slightly lower than that for particles with a smaller size, the difference is still within 16%. The values of \( R_{c,0} \) based on the 0.2 µm Anopore membrane is significantly lower than those based on the 0.2 µm PCTE membrane. This discrepancy is likely due to the different adhesive interaction between the membrane surface and the particles or the different roughness of the membrane surface. We also note that \( R_{c,0} \) based on the 0.2 µm Anopore membrane for the 0.25 µm polystyrene microspheres (9.3×10\(^{9} \) m\(^{-1} \)) is nearly three times larger than that for the 0.54 µm polystyrene microspheres (2.7×10\(^{9} \) m\(^{-1} \)). As introduced in section 3.2.3, Anopore membranes have a much higher membrane porosity (\( \varepsilon_{ms} = 0.6 \)) than that for the PCTE membranes (\( \varepsilon_{ms} = 0.05 \sim 0.20 \)). As the particle with size 0.54 µm was used, the
number of pores covered by one foulant particle \( n_s \) for the 0.2 \( \mu m \) PCTE membrane was 1, while 4 for 0.2 \( \mu m \) Anopore membrane as indicated by Eq. (6.5). However, the 0.54 \( \mu m \) polystyrene microspheres may not be able to completely block all these pores due to their spherical shape. Therefore, some of these pores may still be exposed to the voids of cake layer. We assumed that only one pore could be completely blocked by the particle, and the average \( R_{c0} \) for the case of \( n_s \) larger than one was estimated by:

\[
\frac{1}{R_{c0}} = \frac{1}{n_s} \left( \frac{1}{R_{c0}} + \frac{n_s - 1}{R_{cs}} \right)
\]

(6.22)

where \( R_{cs} \) is the resistance of single layer particle. For a perfect spheroid, \( R_{cs} \) can be calculated by:

\[
R_{cs} = \frac{36(1 - \varepsilon)^2}{\varepsilon^4 r_p}
\]

(6.23)

\( R_{c0} \) estimated based on Eqs. (6.22) and (6.23) is \( 5.3 \times 10^9 \, m^{-1} \) for a 0.54 \( \mu m \) polystyrene microsphere. This value is still larger than the experimental value \( 2.7 \times 10^9 \, m^{-1} \) which probably due to the larger void formed on the membrane surface during the filtration. All these parameters for feed characteristics of polystyrene microspheres were summarized in Table 6.2.

Polystyrene microspheres with sizes of 0.25 \( \mu m \), 0.46 \( \mu m \), and 0.54 \( \mu m \) were all filtered through both 0.2 \( \mu m \) PCTE and Anopore membranes at a transmembrane pressure of 2 psi (PCTE) or 2.5 psi (Anopore). The concentration of polystyrene microsphere solutions was varied from 0.000625 to
0.005 g/L. The experimental results were plotted in Figure 6.7(a) for the PCTE membrane and (b) for the Anopore membrane. It shows that the flux decline rate increased as the particle concentration increased. For the same concentration level, the polystyrene microspheres with smaller size yielded faster decay during the initial filtration compared to the beads with larger size. This is consistent with the sensitivity analysis of $r_p$ (section 6.4.1.1) indicating the positive impact of particle size on the flux decline. Due to the lower initial resistance of a single foulant particle $R_{0}$, the flux decline curves for polystyrene microspheres filtering through Anopore membranes demonstrated a region with concave down curves during the initial filtration as shown in Figure 6.7(b).

The solid curves in Figure 6.7 are the modeling calculations based on the external fouling parameters listed in Table 6.3, which were calculated based on the feed characteristics (Table 6.2) and the membrane properties (Table 3.2). Specially, the membrane surface porosity for the 0.2 µm PCTE membrane was set to 0.15. Clearly, the model predictions are in good agreement with the experimental results. We also note that the model predictions for the 0.25 µm polystyrene microspheres through the 0.2 µm PCTE membranes (Figure 6.7(a1)) yielded faster decay during the initial filtration compared to the experimental data. This is likely due to the fact that some particles may not be deposited on the membrane pores since the PCTE membranes had lower membrane surface porosity.
6.4.2.2 Proteins

In contrast to polystyrene microsphere solutions, protein solutions contain both monomer (or oligomers), whose size is much smaller than the membrane pore size, and large aggregates, which are referred to as the foulant particles. In addition, foulant particles in protein solutions have broader size distribution and irregular shape. Hence, we first determined the particle size distribution and mass fraction of foulant particles in the protein solutions.

The particle size distribution of the protein solutions was obtained by DLS measurements (section 6.3.2). The DLS measurement results were given by relative intensity plots as shown in Figure 6.8(a) for BSA (2 g/L) and (b) for α-casein (0.001 g/L). Figure 6.8(a) shows that the particle size of the BSA monomer (or oligomers) was about 2 nm while the BSA aggregates had a size of 2.5 μm. In contrast, smaller aggregates (about 0.4 μm) were detected in α-casein solution as shown in Figure 6.8(b).

The foulant (Φ ≥ 0.2 μm) mass fraction in the protein solutions was also estimated from the experimental data of the DLS measurements:

\[
f'_{\text{DLS}} = \frac{\sum \xi_{m_i} (\Phi_i \geq 0.2 \mu m)}{\sum \xi_{m_i}}
\]

As introduced in section 3.3.2.2, the relative mass weighted intensity was calculated based on the relative particle number weighted intensity. It was implicitly assumed that the particles were perfect spheroids. However, in the majority of applications,
this assumption is highly unrealistic [261]. When the foulant particles are
nonspheriod, \( f'_\text{DLS} \) may deviate from the actual foulant mass fraction \( f' \). Previous
study [262] showed that the diffusion coefficient of an oblate spheroid could be
correlated with the aspect ratio \( \frac{r_{pc}}{r_{pa}} \) based on the modified Stokes-Einstein equation.

Based on the assumption of an oblate spheroid, we can roughly correlate the particle
volume indicated by DLS \( V_{pDLS} \) with the particle volume \( V_p \) by the aspect ratio:

\[
V_p = V_{pDLS} \frac{r_{pc}}{r_{pa}} \quad (6.25)
\]

As the particle size of the monomer (or oligomor) is much smaller than that of the
foulant particles, it gives:

\[
f'_\text{DLS} = \frac{V_{pDLS}}{V_{sp} + V_{pDLS}} \quad (6.26)
\]

\[
f' = \frac{V_p}{V_{sp} + V_p} \frac{r_{pc}}{r_{pa}} = \frac{V_{pDLS}}{V_{sp} + V_{pDLS}} \frac{r_{pc}}{r_{pa}} \quad (6.27)
\]

where \( V_{sp} \) is the volume of particles with smaller size. It is implicitly assumed that
all particles have the same density. Combining Eqs. (6.26) and (6.27), we can get:

\[
\frac{r_{pc}}{r_{pa}} = \frac{f'(1 - f'_{\text{DLS}})}{f'_{\text{DLS}}(1 - f') \quad (6.28)}
\]

With Eq. (6.28), the aspect ratio \( \frac{r_{pc}}{r_{pa}} \) was estimated for the protein aggregates
based on the experimental data of both DLS (\( f'_{\text{DLS}} \)) and filtration (\( f' \)). As shown in
Figure 6.8(a), \( f'_{\text{DLS}} \) for BSA was determined to be 0.015. \( f' \) measured by
weighing the fouled membranes (section 6.3.2) was 0.006. This discrepancy can be roughly attributed to the nonspherical shape of the BSA protein aggregates as the large aggregates may have lower density compared to the monomers. Then, \( \frac{r_{pc}}{r_{pa}} \) for the BSA aggregates can be calculated to be 0.4 based on Eq. (6.28).

In contrast to BSA solutions, \( f'_{DLS} \) determined for \( \alpha \)-casein is 0.85, which is very close to the value of \( f' \) 0.81. The calculated \( \frac{r_{pc}}{r_{pa}} \) for \( \alpha \)-casein is 0.75. It indicates that \( \alpha \)-casein aggregates have higher sphericity than that of BSA aggregates. This is consistent with the fact reported in earlier studies [263, 264] that \( \alpha \)-casein maybe present as spherical micelles in the aqueous solutions.

The porosity of the protein cake layer and the initial resistance of the single protein aggregate based on the 0.2 \( \mu \)m PCTE membrane were determined by measuring \( R_{total} \) as a function of filtrate volume as introduced in section 6.3.2. \( \varepsilon_c \) for BSA was calculated as 0.19, and 0.24 for \( \alpha \)-casein. This is consistent with the earlier study [265] that the packing of an oblate spheroid with lower aspect ratio yields a higher packing density (lower porosity). The trendline intercept of \( R_{total} - R_m \) versus \( V \) (Figure 6.9) determined \( R_{c0} \) for BSA as 3.3\( \times 10^{10} \) \( m^{-1} \) and 4.2\( \times 10^{11} \) \( m^{-1} \) for \( \alpha \)-casein. As revealed by previous studies [266, 267], \( \alpha \)-casein is an amphiphilic protein, thereby presenting as micelles with hydrophilic functional groups exposed to the aqueous surroundings. As a result, the surface caseins in the micelle are almost certainly not adsorbed in the same way as the proteins are adsorbed to hydrophobic interfaces [267], like BSA. This explains why \( R_{c0} \) for \( \alpha \)-casein
was significantly higher than that for BSA based on hydrophilic PCTE membranes. In addition, we also note that the particle size of α-casein (0.4 μm) is relatively close to the membrane pore size (0.2 μm) compared to BSA (2.5 μm). This may result in tighter blockage when the membrane is covered by α-casein aggregates.

Figure 6.10 shows the SEM images of surface (a) and cross-section (b) of the 0.22 μm PVDF membrane fouled by BSA solutions (2 g/L, 2 h, and 2 psi). The particle size of BSA aggregates shown by the SEM image (Figure 6.10(a)) is about 3 μm, which is consistent with the results from DLS measurements (2.5 μm). However, it is difficult to distinguish the fouling layer from the image of cross-section (Figure 6.10(b)) probably due to the denaturing of the protein during the sample preparation. All these parameters for both BSA and α-casein were summarized and listed in Table 6.2.

Both BSA and α-casein solutions were filtered through 0.2 μm PCTE membranes at a transmembrane pressure of 2 psi. The concentration of BSA was varied from 1 to 8 g/L, while the concentration of α-casein ranged from 0.0005 to 0.004 g/L. The bulk concentration of α-casein was much lower than that for BSA due to a higher mass fraction of foulant particles of α-casein solutions as discussed in an earlier section. The experimental data were plotted in Figure 6.11(a) for BSA and (b) for α-casein. The solid curves are model predictions based on the external fouling parameters listed in Table 6.3, which were calculated based on the feed characteristics (Table 6.2) and the membrane properties (Table 3.2). The model predictions show good agreement with the experimental results. It is demonstrated
that α-casein solutions yielded drastic flux decay compared to BSA since the α-casein aggregates have a relatively high $R_{c0}$ and smaller particle size, which results in a higher cake layer resistance as indicated by Eq. (6.18).

### 6.4.3 Model Validation with Binary Mixtures

In this section, we validated our models with binary mixtures, including 0.25 µm polystyrene microspheres mixed with 0.54 µm polystyrene microspheres, 0.25 µm polystyrene microspheres mixed with BSA, and 0.25 µm polystyrene microspheres mixed with α-casein. The external fouling parameters for the single component solutions were used to estimate the fouling parameters for binary mixtures based on the binary mixture rules. Then, the model predictions were compared with the experimental data.

The binary mixture rule for the pore blockage parameter $\alpha$ was given by Eq. (6.7). The specific resistance of the cake layer $R'$ was related to the specific volume based on the particle surface area $S_v$, particle density $\rho_p$, and cake layer porosity $\varepsilon_c$. The mixture rule for $S_v$ accounting for the particle polydispersity was demonstrated in Table 6.1, and the average particle density was evaluated by Eq. (6.17). In previous studies [268], an empirical model for predicting the voidage of binary particle mixtures accounting for particle nonsphericity was provided. We assumed that $R_{c0}$ for mixtures is equal to the area weighted average of $R_{c0}$:

$$\frac{1}{R_{c0}} = \sum_i \frac{\theta_{pi}}{R_{c0i}}$$  (6.29)
where $\theta_p$ is the area fraction based on the blocked area. All these binary mixture rules were summarized and listed in Table 6.4.

6.4.3.1 Binary Mixtures Containing Different Sized Polystyrene Microspheres

First, 0.25 $\mu m$ polystyrene microspheres were mixed with 0.54 $\mu m$ polystyrene microspheres. In this case, both foulant particles are perfect spheroids. In terms of the binary mixture rules listed in Table 6.4, we first calculated the fouling parameters for the binary mixtures containing both 0.25 $\mu m$ and 0.54 $\mu m$ polystyrene microspheres as a function of mass fraction of 0.25 $\mu m$ polystyrene microspheres based on the fouling parameters for a single component listed in Table 6.2 and Table 6.3. The model calculation results were shown in Figure 6.12 (a) for $\alpha$, (b) for $R'$, and (c) for $R_{c0}$.

In Figure 6.12(a), $\alpha$ for the binary mixture is linearly increased from the value for pure 0.54 $\mu m$ polystyrene microspheres ($2.4 \times 10^3 \text{ m}^2/\text{kg}$) to the value for pure 0.25 $\mu m$ polystyrene microspheres ($2.4 \times 10^4 \text{ m}^2/\text{kg}$) as the mass fraction of 0.25 $\mu m$ polystyrene microspheres increased. A maximum was demonstrated in Figure 6.12 (b) for the average $R'$ when the mass fraction of the 0.25 $\mu m$ polystyrene microspheres was about 0.7. This is due to the lowest voidage ($\varepsilon_c$) yielded by the binary mixtures containing different sized particles as indicated by the equation for the average $\varepsilon_c$ in Table 6.4. Figure 6.12(c) shows that the composition variation of the binary mixtures had little impact on the average $R_{c0}$ since both particles had the similar $R_{c0}$ as shown in Table 6.2.
The experimental results of binary mixtures containing both 0.25 μm and 0.54 μm polystyrene microspheres filtering through 0.2 μm PCTE membranes (Δp = 2 psi) were plotted in Figure 6.13. To eliminate the effects of particle concentration on the flux decline, the total foulant particle concentration was fixed at 0.00125 g/L while the mass fraction of 0.25 μm polystyrene microspheres was varied from 0 to 1. It shows that the flux decline rate was decreased as the mass fraction of 0.25 μm polystyrene microspheres increased. The solid curves are the model predictions based on the fouling parameters for single component using the binary mixture rules. The model predictions are in good agreement with the experimental data. On the other hand, the best fit fouling parameters from the experimental data in Figure 6.13 were also plotted as open squares in Figure 6.12 to compare with the calculated fouling parameters based on the binary mixture rules. The best fit $R'$ did not demonstrate a significant maximum as predicted by the mixture rules. This is likely due to that the cake layer formed by binary mixtures was not perfectly uniform.

6.4.3.2 Binary Mixtures Containing Polystyrene Microspheres and BSA

In the second system, 0.25 μm polystyrene microspheres were mixed with BSA. As the external fouling is primarily attributed to the large aggregates in the protein solutions, specially, the mass fraction of the single component is defined based on the total foulant mass in the binary mixtures.

With the parameters for single components as listed in Table 6.2 and Table 6.3,
we calculated the external fouling parameters for the binary mixtures containing both 0.25 \( \mu m \) polystyrene microspheres and BSA based on the binary mixture rules listed in Table 6.4. The calculation results were plotted in Figure 6.14. It shows that \( \alpha \) for the binary mixtures was linearly increased from \( 1.1 \times 10^3 \, m^2/kg \) (pure BSA) to \( 2.4 \times 10^4 \, m^2/kg \) (pure 0.25 \( \mu m \) polystyrene microspheres) as the mass fraction of 0.25 \( \mu m \) polystyrene microspheres increased (Figure 6.14(a)). In Figure 6.14(b), the value of average \( R' \) reached a maximum of \( 1.7 \times 10^{14} \, m/kg \), which was significantly larger than the values for both pure BSA and 0.25 \( \mu m \) polystyrene microspheres, when the mass fraction of the 0.25 \( \mu m \) polystyrene microspheres is about 0.2. This is due to the relatively low particle size ratio \( \frac{r_{pPS}}{r_{pBSA}} = 0.14 \) of this binary mixture as indicated by the equations for the average \( \varepsilon_c \) in Table 6.4. As the BSA aggregates have a higher \( R_{c0} \) (3.3\( \times 10^{10} \, m^{-1} \)) than that for the 0.25 \( \mu m \) polystyrene microspheres (1.8\( \times 10^{10} \, m^{-1} \)), the average \( R_{c0} \) for the binary mixtures is monotonically decreasing as the mass fraction of 0.25 \( \mu m \) polystyrene microspheres increased (Figure 6.14(c)).

The binary mixtures containing both 0.25 \( \mu m \) polystyrene microspheres and BSA were filtered through 0.2 \( \mu m \) PCTE membranes at a transmembrane pressure of 2 \( psi \). To eliminate the effects of particle concentration on the flux decline, the total foulant particle (\( r_p \geq 0.2 \, \mu m \)) concentration was fixed at 0.00125 g/L while the mass fraction based on the total foulant mass of 0.25 \( \mu m \) polystyrene microspheres was varied from 0 to 1. The experimental results were plotted in
Figure 6.15. The solid curves are the model predictions based on the fouling parameters for single component with the binary mixture rules. The model predictions show a relatively weak correlation with the experimental data compared to the results of different sized polystyrene microspheres as shown in Figure 6.13. It shows that the present of 0.25 μm polystyrene microspheres in the binary mixtures yielded a drastic flux decay compared to the flux decline rate of pure BSA solutions. As the mass fraction of 0.25 μm polystyrene microspheres increased, the rate of flux decline was reduced.

The best fit fouling parameters from the experimental data in 6.15 were also plotted as open squares in Figure 6.14 to compare with the calculated fouling parameters based on the binary mixture rules. It shows a positive deviation of the best fit $\alpha$ (Figure 6.14(a)) and a negative deviation of the best fit $R'$ (Figure 6.14(b)) from the model predictions. This discrepancy is due to the fact that the large BSA aggregates were prevented from reaching the membrane surface, and rejected in the upper part of the cake layer as indicated by the SEM images (Figure 6.16). The best fit $R_{c,0}$ was significantly larger than the model predictions as shown in Figure 6.14(c). This can be explained by the fact that BSA is prone to be adsorbed onto the polystyrene microspheres with a hydrophobic surface as indicated by previous studies [269, 270]. The adsorption of BSA onto the polystyrene microspheres changed the interaction between the polystyrene microspheres and the membrane, thereby causing a higher initial resistance.
6.4.3.3 Binary Mixtures Containing Polystyrene Microspheres and α-Casein

As discussed in section 6.4.2.2, the characteristics of α-casein are significantly different from BSA. The particle size of α-casein aggregates (0.4 \( \mu m \)) is closer to the particle size of the polystyrene microspheres used in this study. Here, we mixed α-casein with 0.25 \( \mu m \) polystyrene microspheres to form the binary mixtures with various compositions. Again, the mass fraction was calculated based on the total mass of foulant particles in the binary mixtures.

Similarly, with the parameters in Table 6.2 and Table 6.3, we can calculate the external fouling parameters for the binary mixtures containing 0.25 \( \mu m \) polystyrene microspheres and α-casein based on the binary mixture rules listed in Table 6.4. All calculation results were plotted in Figure 6.17 as solid curves. It is demonstrated in Figure 6.17(a) that \( \alpha \) for the binary mixtures linearly increased from 6.4×10\(^3\) m\(^2\)/kg (pure α-casein) to 2.4×10\(^4\) m\(^2\)/kg (pure 0.25 \( \mu m \) polystyrene microspheres) as the mass fraction of 0.25 \( \mu m \) polystyrene microspheres increased. As α-casein aggregates had a similar size to that of the 0.25 \( \mu m \) polystyrene microspheres, in Figure 6.17(b), the binary mixtures did not yield a maximum of \( R' \), which was shown in Figure 6.13(b) and Figure 6.15(b). The value of the average \( R' \) monotonically decreased as the mass fraction of 0.25 \( \mu m \) polystyrene microspheres increased. It is interesting to note that the value of \( R_{e0} \) for the binary mixtures was dramatically decreased from 4.2×10\(^{11}\) m\(^{-1}\) (for pure α-casein) to about 5×10\(^{10}\) m\(^{-1}\) when the mass fraction of 0.25 \( \mu m \) polystyrene microspheres was increased to 0.2 as shown in Figure 6.17(c).
The flux decline was measured by filtering the binary mixtures containing both the 0.25 μm polystyrene microspheres and α-casein through 0.2 μm PCTE membranes at a transmembrane pressure of 2 psi. The total concentration of foulant particles in the binary mixtures was fixed at 0.00125 g/L while the mass fraction of the 0.25 μm polystyrene microspheres was varied from 0 to 1. The experimental results were plotted in Figure 6.18, and the solid curves represent the model predictions based on the parameters for single components (Table 6.2 and Table 6.3). Clearly, the model predictions are consistent with the experimental results. It shows that the flux decline rate was significantly decreased as the mass fraction of 0.25 μm polystyrene microspheres increased.

The best fit fouling parameters based on the experimental data in Figure 6.18 were plotted as open squares in Figure 6.17 to compare with the calculated fouling parameters based on the binary mixture rules (Table 6.4). The model predictions are in good agreement with the best fit results. The value of the best fit $R_{c0}$ was slightly higher than the predicted value when the mass fraction of the 0.25 μm polystyrene microspheres is lower than 0.4. This is likely due to the fact that more α-casein aggregates were adsorbed onto the membrane surface during the filtration.

### 6.5 Conclusions

In this study, we demonstrated that the fouling parameters in the combined fouling model accounting for both pore blockage and cake filtration could be estimated based on the feed characteristics and the membrane properties. The
mathematical correlations between the fouling parameters and the parameters of feed characteristics and membrane properties were developed based on the physical meaning of the fouling parameters. These mathematical models had more degrees of freedom to predict complex systems.

The estimation of the fouling parameters based the developed models was validated by single component solutions, including different sized polystyrene microspheres, and proteins (BSA and α-casein). The feed characteristics for each system were determined with independent experiments, and were used to calculate the fouling parameters. The model predictions are in good agreement with the experimental results of flux decline measurements.

In order to predict the fouling behavior of the complex mixtures, the binary mixture rules for predicting the fouling parameters for the binary mixtures with the fouling parameters from single components were developed. The model predictions were validated by various binary mixtures, including: i) 0.25 \( \mu m \) polystyrene microspheres mixed with 0.54 \( \mu m \) polystyrene microspheres; ii) 0.25 \( \mu m \) polystyrene microspheres mixed with BSA; iii) 0.25 \( \mu m \) polystyrene microspheres mixed with α-casein. The model predictions are consistent with the experimental results of each system.

These studies indicate that the external fouling parameters can be predicted in terms of the feed characteristics and membrane properties for both single component solutions and binary mixtures. This provides deep insights regarding the mechanisms of external fouling during the microfiltration processes.
Table 6.1 Equations for $S_V$ Accounting for the Particle Polydispersity

<table>
<thead>
<tr>
<th></th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spheroid</td>
<td>$\frac{3}{r_p}$</td>
</tr>
<tr>
<td></td>
<td>$+ \arctan h \left[ \sin \left( \arccos \frac{r_{pc}}{r_{pa}} \right) \right]$</td>
</tr>
<tr>
<td></td>
<td>$= \frac{3}{2} \left( \frac{r_{pa}^2}{r_{pc}} - \frac{r_{pc}^2}{r_{pa}} \right)$</td>
</tr>
<tr>
<td>Oblate spheroid</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixture</td>
<td>$\sum_i \frac{\omega_i}{\rho_i} \frac{S_{vi}}{\bar{\rho}_p}$</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th></th>
<th>$f'$</th>
<th>$f_{DLS}'$</th>
<th>$r_{pa}$ (µm)</th>
<th>$r_{pc}$ [3] (µm)</th>
<th>$r_p$ [3] (µm)</th>
<th>$S_v$ [3]</th>
<th>$\rho_p$ [2] (kg/m³)</th>
<th>$\varepsilon_c$ [1]</th>
<th>$R_{\varepsilon 0}$ [1] (based on 0.2 µm PCTE) (m⁻¹)</th>
<th>$R_{\varepsilon 0}$ [1] (based on Anopore) (m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.25$ µm PS Bead</td>
<td>1</td>
<td>1</td>
<td>0.125</td>
<td>0.125</td>
<td>0.125</td>
<td>24</td>
<td>$1.05 \times 10^3$</td>
<td>0.34</td>
<td>$1.8 \times 10^{10}$</td>
<td>$9.3 \times 10^{9}$</td>
</tr>
<tr>
<td>$0.46$ µm PS Bead</td>
<td>1</td>
<td>1</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
<td>13</td>
<td>$1.05 \times 10^3$</td>
<td>0.34</td>
<td>$1.6 \times 10^{10}$</td>
<td>$4.1 \times 10^{9}$</td>
</tr>
<tr>
<td>$0.54$ µm PS Bead</td>
<td>1</td>
<td>1</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>11.1</td>
<td>$1.05 \times 10^3$</td>
<td>0.34</td>
<td>$1.5 \times 10^{10}$</td>
<td>$2.7 \times 10^{9}$</td>
</tr>
<tr>
<td>BSA</td>
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<td>0.015 [1]</td>
<td>1.25 [1]</td>
<td>0.5</td>
<td>0.92</td>
<td>3.8</td>
<td>$1.35 \times 10^3$</td>
<td>0.19</td>
<td>$3.3 \times 10^{10}$</td>
<td></td>
</tr>
<tr>
<td>α-Casein</td>
<td>0.81 [1]</td>
<td>0.85 [1]</td>
<td>0.2 [1]</td>
<td>0.15</td>
<td>0.18</td>
<td>16.7</td>
<td>$1.29 \times 10^3$</td>
<td>0.24</td>
<td>$4.2 \times 10^{11}$</td>
<td></td>
</tr>
</tbody>
</table>

[1]. Experimental values
[2]. Density values for BSA and α-casein are from references [271] and [272], respectively.
[3]. Calculated values
Table 6.3 Calculated Fouling Parameters Based on the Feed Characteristics in Table 6.2

<table>
<thead>
<tr>
<th>Feed</th>
<th>0.2 μm PCTE ($\varepsilon_{ms} = 0.15$)</th>
<th>0.2 μm Anopore ($\varepsilon_{ms} = 0.60$)</th>
<th>$R'$</th>
<th>$fR'$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n_s$</td>
<td>$\alpha$ (m$^2$/kg)</td>
<td>$f'\alpha$ (m$^2$/kg)</td>
<td>$n_s$</td>
</tr>
<tr>
<td>0.25 μm PS Bead</td>
<td>1</td>
<td>2.4×10$^4$</td>
<td>2.4×10$^4$</td>
<td>1</td>
</tr>
<tr>
<td>0.46 μm PS Bead</td>
<td>1</td>
<td>3.9×10$^3$</td>
<td>3.9×10$^3$</td>
<td>3</td>
</tr>
<tr>
<td>0.54 μm PS Bead</td>
<td>1</td>
<td>2.4×10$^3$</td>
<td>2.4×10$^3$</td>
<td>4</td>
</tr>
<tr>
<td>BSA</td>
<td>23</td>
<td>1.1×10$^3$</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>α-Casein</td>
<td>1</td>
<td>6.4×10$^3$</td>
<td>5.2×10$^3$</td>
<td></td>
</tr>
</tbody>
</table>
### Table 6.4 Binary Mixture Rules for Fouling Parameters

<table>
<thead>
<tr>
<th>Fouling Parameter</th>
<th>Binary Mixture Rules$^{[1]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>$\omega_1\alpha_1 + \omega_2\alpha_2$</td>
</tr>
</tbody>
</table>

\[
\frac{\bar{S}_v}{\bar{V}_s} = \left(\frac{\bar{V}_s^2 - \omega_1\omega_2}{V_1}\right) + 2\left(\frac{\bar{V}_s - \omega_1\omega_2}{V_1}\right) + \left(\frac{\bar{V}_s - \omega_1\omega_2 - \omega_1\omega_1}{V_2 - 1}\right) = 1,
\]

\[
\frac{2(1 - \bar{c}^2)}{\bar{c}^2\bar{\rho}} \bar{S}_v^2
\]

\[\bar{\epsilon}_c = \bar{V}' = \frac{1}{1 - \bar{c}^2}\]

\[R' = 1.355 \left(\frac{r_{pa1}}{r_{pa2}}\right)^{1.566} \left[r_{pa1} \leq 0.824\right], \quad r_{pa} = \left[3.178 - \frac{3.682}{\phi_s} + \frac{1.504}{\phi_s^2}\right] r_p
\]

\[\frac{\bar{r}_p}{\bar{r}_p} = \frac{\omega_1}{\omega_1 + \omega_2}\]

\[R_{c_0} = \frac{\theta_{p1}}{R_{c_01}} + \frac{\theta_{p2}}{R_{c_02}}\]

$[1]$. Index 1 represents the particle with smaller size, index 2 represents the particle with larger size;

$[2]$. Provided by Ref. [268]
Figure 6.1 Schematic diagram of the shape of foulant particle a) ellipsoid b) sphere.
Figure 6.2 Sensitivity analysis of feed characteristics: a) particle size b) particle aspect ratio c) particle density d) cake layer porosity

\( \Delta p = 2 \text{ psi}, C_b = 0.0005 \text{ g/L}, r_p = 0.25 \mu m, \rho_p = 1.05 \times 10^3 \text{ kg/m}^3, \Phi_S = 1, \epsilon_c = 0.25, r_m = 0.2 \mu m, \epsilon_{ms} = 0.15, R_m = 5 \times 10^{10} \text{ m}^{-1}, R_{co} = 2 \times 10^{10} \text{ m}^{-1} \).
Figure 6.3 Sensitivity analysis of membrane properties: a) membrane pore size b) membrane surface porosity ($\Delta p=2$ psi, $C_b=0.0005$ g/L, $r_p=0.25$ $\mu$m, $\rho_p=1.05 \times 10^3$ kg/m$^3$, $\Phi_b=1$, $\epsilon_c=0.25$, $r_m=0.2$ $\mu$m, $\epsilon_{ms}=0.15$, $R_m=5 \times 10^{10}$ m$^{-1}$, $R_o=2 \times 10^{10}$ m$^{-1}$).
Figure 6.4 Sensitivity analysis of lumped parameters: a) number of covered pores per particle b) the resistance ratio of single particle to membrane ($\Delta p=2$ psi, $C_b=0.0005$ g/L, $r_p=0.25$ $\mu$m, $\rho_p=1.05 \times 10^3$ kg/m$^3$, $\Phi_S=1$, $\epsilon_c=0.25$, $r_m=0.2$ $\mu$m, $\epsilon_{ms}=0.15$, $R_m=5 \times 10^{10}$ m$^{-1}$, $R_{c0}=2 \times 10^{10}$ m$^{-1}$).
Figure 6.5 Experimental data fitting of hydraulic resistance of cake layer: a) PS beads on 0.2 µm PCTE b) PS beads on 0.2 µm Anopore.
Figure 6.6 Scanning electron micrographs of the cake layer formed by depositing 0.46 µm PS beads 0.22 µm PVDF membrane surface (C₀=0.002 g/L, V=600 mL, Δp=2 psi): a) cake layer surface b) cake layer cross-section.
Figure 6.7 Different sized PS beads filtered through a) 0.2 µm PCTE (Δp=2 psi) and b) 0.2 µm Anopore (Δp=2.5psi). Solid curves are model calculations based on the parameters in Table 6.3.
Figure 6.8 Relative intensity of particle mass measured by dynamic light scattering: a) BSA ($C_b=2 \text{ g/L}$) b) $\alpha$-casein ($C_b=0.001 \text{ g/L}$).
Figure 6.9 Experimental data fitting of hydraulic resistance of cake layer: a) BSA + 0.2 µm PCTE b) α-Casein + 0.2 µm PCTE.
Figure 6.10 Scanning electron micrographs of the cake layer formed by filtering BSA through 0.22 µm PVDF membrane ($C_b=2$ g/L, 2 h, $\Delta p=2$ psi): a) cake layer surface b) cake layer cross-section.
Figure 6.11 Protein solutions filtered through 0.2 µm PCTE (Δp=2 psi): a) BSA b) α-Casein. Solid curves are model calculations based on the parameters in Table 6.3.
Figure 6.12 Fouling parameters of the binary mixtures containing 0.25 µm and 0.54 µm PS beads as a function of mass fraction of 0.25 µm PS beads: a) pore blockage parameter α b) specific resistance of cake layer $R'$ c) initial resistance of single foulant $R_{c0}$. Solid curves are model calculations based on the parameters in Table 6.3 and binary mixture rules, open squares are best fit results from filtration experiments.
Figure 6.13 Binary mixtures containing 0.25 μm and 0.54 μm PS beads filtered through 0.2 μm PCTE (Δp=2 psi) with the total foulant concentration $C'_b=0.00125$ g/L while varying the mass fraction of 0.25 μm PS beads from 0 to 1. Solid curves are model calculations based on the parameters in Table 6.3 and binary mixture rules, solid circles are experimental results.
Figure 6.14 Fouling parameters of the binary mixtures containing 0.25 µm and BSA as a function of mass fraction of 0.25 µm PS beads: a) pore blockage parameter $\alpha$, b) specific resistance of cake layer $R'$, c) initial resistance of single foulant $R_{c0}$. Solid curves are model calculations based on the parameters in Table 6.3 and binary mixture rules, open squares are best fit results from filtration experiments.
Figure 6.15 Binary mixtures containing 0.25 µm and BSA filtered through 0.2 µm PCTE ($\Delta p=2$ psi) with the total foulant concentration $C'_b=0.00125$ g/L while varying the mass fraction of 0.25 µm PS beads from 0 to 1. Solid curves are model calculations based on the parameters in Table 6.3 and binary mixture rules, solid circles are experimental results.
Figure 6.16 Scanning electron micrographs of the cake layer formed by filtering binary mixtures containing 0.25 µm PS beads (C_b=0.001 g/L) and BSA (C_b=1 g/L) through 0.2 µm PCTE membrane surface (2 h, Δp=2 psi): a) cake layer surface b) the magnified portion of cake layer surface.
Figure 6.17 Fouling parameters of the binary mixtures containing 0.25 µm and α-casein as a function of mass fraction of 0.25 µm PS beads: a) pore blockage parameter $\alpha$ b) specific resistance of cake layer $R'$ c) initial resistance of single foulant $R_{c0}$. Solid curves are model calculations based on the parameters in Table 6.3 and binary mixture rules, open squares are best fit results from filtration experiments.
Figure 6.18 Binary mixtures containing 0.25 µm and α-casein filtered through 0.2 µm PCTE (Δp=2 psi) with the total foulant concentration $C'_b=0.00125$ g/L while varying the mass fraction of 0.25 µm PS beads from 0 to 1. Solid curves are model calculations based on the parameters in Table 6.3 and binary mixture rules, solid circles are experimental results.
7.1 Introduction

In the previous sections, we demonstrated that the fouling behavior could be described by the mathematical models accounting for various fouling mechanisms and membrane morphology. All these fouling models rely on the macroscopic continuum conservation equation, and the fouling rate was correlated to the differential equations indicating the mass balance for both space and time. Although these continuum approaches yielded good agreement between the theory and the experiments, there are still some discrepancies which could not be explained by the conventional ways. This is because some exact details concerning particle transport and membrane structure were ignored or lumped into some phenomenological coefficients.

For example, the pore constriction model attributes the reduction of permeability to the shrinkage of void volume. In order to get an explicitly analytical solution, it was assumed that the membrane has straight-through cylindrical pores, and the foulant particles are uniformly adsorbed onto the pore walls. However, some studies [273, 274] found that the particles could uniformly deposit only over the inlet portion of the pore walls, and the membrane selectivity was not constant during the filtration. Ramachandran et al. [275] showed that particle retention can occur due to
the hydrodynamic bridging when the particles have small size relative to the pore size, and the particle-pore surface electrostatic repulsion prevents deposition. The conventional approaches are unable to predict this fouling behavior which involves the understanding at the pore scale or particle scale.

The mathematical model developed by Ho and Zydney [124] accounted for the membrane morphology by characterizing the pore connectivity as the permeability ratio of the horizontal direction to the transverse direction. This model successfully explained the discrepancy of flux decline between the membrane with straight-through pores and the membrane with highly interconnected pores when external fouling was dominant. As being able to evaluate the normalized flow rate for a given permeability profile when internal retention occurs, this model cannot predict the foulant particle distribution within the membrane structures since the exact membrane structures are lumped into the permeability coefficients.

Network modeling is a useful tool for investigating pore-scale or particle-scale behavior, and also provides a bridge from the pore to the continuum scale. For example, Balhoff et al. [276] investigated the flow through a heterogeneous packed bed by coupling the network to the continuum-scale models. As discussed in section 1.3.2, being a statistical approach, network modeling relies on a more realistic representation of the pore structures, and usually requires much more computational effort in contrast to the continuum approaches.

Although network modeling has been widely applied to a variety of fields involving particle flow through porous media, only a few studies implementing this
approach for membrane fouling have been reported. Davies and Jia [173] employed both a sphere packing model and a random network model to simulate the filtration of granular membranes when cake filtration or internal fouling is important. In this modeling, the fouling mechanisms for both cake filtration and internal fouling were explicitly described at a pore scale, and the change of the network permeability versus operation time was investigated. With the network approach, Duclos-Orsello et al. [175] tried to design a membrane with high retention by adsorption via attractive particle-surface interactions. These studies were focused on the effects of particle size, pore size, and ionic strength on adsorptive particle retention, and the particle capture based on size exclusion was ignored since the studied particles were much smaller than the filter size.

In CHAPTER 6, we studied the pore blockage and cake filtration at a particle scale, and correlated the fouling parameters in the continuum-scale models with the feed characteristics and membrane properties. However, the membranes were still assumed to be homogeneous with straight-through cylindrical pores. Therefore, in this section, we investigated the membrane fouling at a pore scale with the network approach. The membranes with various morphologies were represented by a three-dimensional network with proper structure parameters. The fouling behavior was attributed to particle straining, particle trapping, and particle packing. The model predictions were validated by the filtration experiments, which were designed to make a fouling mechanism dominate the fouling process, and compared with the results based on the conventional fouling models.
7.2 Model Development

In contrast to the other modeling based on the network approach, like deep bed filtration, the simulation of fouling processes mainly deals with three problems as mentioned in section 1.3.2: i) how to construct a network representing a given membrane structure; ii) how to describe the capture of the foulant particles; iii) how to evaluate the properties of the network fouled by foulant particles.

7.2.1 Network Construction

A network for the simulation of membrane fouling should be able to account for all primary membrane properties, including membrane thickness, membrane pore size, pore size distribution, pore shape, pore connectivity, and so on. Specially, in the current study, we only account for the homogeneous membranes, and the asymmetric membrane structures will be discussed in the next chapter.

7.2.1.1 Geometrical Configuration

A three-dimensional network with coordinate number $Z$ of 6 was adopted in our studies. Figure 7.1 schematically shows the lattice structure of this cubic network. Although more complicated approaches using a bond-site network were developed for estimating the porosimetry curves [192], we adopted the bond-only regular cubic matrix due to the limitation of computational ability. In Figure 7.1, the lines represent the bonds, and their intersection is called node, for which the volume is
assumed to be zero in this network.

The coordinate system for this network is defined by specifying the horizontal direction as \( x \) and \( y \), and the transverse direction as \( z \). The dashed lines indicate the periodic boundary for the network in both the \( x \) and \( y \) directions. In the transverse direction, the network is naturally separated into many layers numbered by \( n_e \). The entry of the network is located at the first network layer, and represented by an array of hypothetical bonds of which size is identical with the \( z \) bonds of the first network layer. We defined the site as the region around a certain node, and the sites of each layer are numbered by \( n_{ex} \) and \( n_{ey} \) for \( x \) and \( y \) directions, respectively. In order to avoid the trajectory analysis, which involves solving complicated differential equations, we defined the bond in our network as a straight-through cylindrical tube with radius of \( r_b \).

7.2.1.2 Structure Parameters

The length of the \( z \) bonds is denoted by \( L_{zc} \). Specially, in the current model, we assumed that all network layers share the same bond length. Therefore, it yields

\[
L_m = n_{ez} L_{zc}
\]  \hspace{1cm} (7.1)

For a given membrane thickness \( L_m \), it indicates that the length of the \( z \) bond is inversely proportional to the number of network layers. In order to account for the particle distribution along the membrane profile, we usually assign \( L_{zc} \) a value of the same order of magnitude with the maximum membrane pore size.
Specially, we assumed that $L_{bx}$ and $L_{by}$ share the same value. We also assumed that the $z$ bond density $\dot{n}_{bz}$ (number of $z$ bonds per network area) has the same order of magnitude as the membrane pore density (number of membrane pores per membrane area) yielding:

$$\frac{\pi \bar{r}_m^2}{L_{bx} L_{by}} = o(\epsilon_{ms})$$  \hspace{1cm} (7.2)$$

where $\epsilon_{ms}$ is the membrane surface porosity, and $\bar{r}_m$ is the average membrane pore size, which is also equivalent to the average bond size $\bar{r}_b$ in this model.

The bond size distribution is approximated by a log-normal probability density function as shown in Eq. (1.42). Specially, we defined $\eta_b$ as the ratio of standard deviation $\sigma_m$ to the average bond size $\bar{r}_b$:

$$\eta_b = \frac{\sigma_m}{\bar{r}_b}$$  \hspace{1cm} (7.3)$$

For given $\bar{r}_b$ and $\eta_b$, the bond size can be calculated based on Eq. (1.42), and assigned to each bond in the network.

We accounted for both size-induced and connectivity-induced anisotropy [277] by defining:

$$\varphi_x = \frac{\bar{r}_{bx}}{\bar{r}_{bc}}$$  \hspace{1cm} (7.4)$$

$$\varphi_y = \frac{\dot{n}_{bx}}{\dot{n}_{bc}}$$  \hspace{1cm} (7.5)$$

where the subscript $h$ denotes $x$ or $y$. A bond is set to be disconnected by
assigning the bond size zero.

### 7.2.2 Particle Flow

The number of particles injected to the network per filtration interval is determined by:

\[
\frac{C_3 Q \Delta t}{4 \frac{4}{3} \pi r_p^3 \rho_p}
\]  

(7.6)

In the current model, we implicitly assumed that all particles had uniform size. During a certain filtration interval, a steady state was assumed so that we could run these particles one by one without changing the fluid flow. The interaction between the particles was ignored as dilute solutions were investigated in the current studies.

#### 7.2.2.1 Particles outside Network

As a particle is injected to the network, first, a surface site as the entry is selected randomly, but with a bias toward the paths with higher flow rates. This rule is called flow-biased probability [186].

If the particle size is smaller than the entry bond size of the selected site, it enters the network. On the other hand, for the particles with larger size compared to the bond size, the status of the selected site need to be checked to determine whether this particle is strained or packed. If the selected site is open, the particle is strained on the network surface; if the selected site has been blocked by other particles, this particle is packed on the blocked site to form a cake layer.
Specially, when the size of particles is much larger than the size of a site \((L_{hx}, L_{hy})\), more than one site are covered by a particle. The number of covered sites \(n_{cs}\) can be estimated by:

\[
 n_{cs} = \text{round} \left[ \frac{1}{L_{hx} L_{hy}} \left( \frac{4 \pi r_p^3}{3 (1 - \varepsilon_{cs})^2} \right) \right] \tag{7.7}
\]

A spiral distribution rule was adopted so that these \(n_{cs}\) sites could be arranged with the most concentrated topology as shown in Figure 7.2. We also assumed that only the site selected by the flow-biased probability was completely blocked by the particle.

### 7.2.2.2 Particles inside Network

As revealed by previous studies [206], even for large ratios of particle size to bond size (as high as 0.95) the deviation of the particle velocity from the average fluid velocity is negligible. Hence, we run the particles through the network bonds with the average velocity of the fluid within that bond.

The flow-biased probability is applied again to determining an exit path when a particle arrives at a node within the network. Obviously, the exit paths are those bonds with fluid flow leaving that node. If all exit paths have been blocked, this particle will be packed to form an internal cake layer as shown in Figure 7.3.

In most previous studies, the particles were strained at the entry of the selected bond as shown in Figure 7.3 as long as the particle size was larger than the size of that bond, and the blocked bonds were set to be completely disconnected. Here, we
modified the test of torque balance for particles on the wall with protrusions [211] to
determine whether the bond is able to strain that particle with a larger size. In this
test, a critical velocity for the tangential flow was first determined by the torque
balance on the particle:

\[ F_N r_b = F_T \sqrt{r_p^2 - r_b^2} + M_T \]  \hspace{1cm} (7.8)

where \( F_N \) and \( F_T \) are the net drag forces acting on the particle by the normal flow
and tangential flow, respectively, \( M_T \) is the moment around the center of the particle
resulting from fluid drag. This torque balance was schematically shown in Figure
7.4(a). These drag forces and moment can be related to the particle size and fluid
velocity as [278, 279]:

\[ F_N = 10.205 \pi \mu r_p v_N \]  \hspace{1cm} (7.9)

\[ F_T = 10.205 \pi \mu r_p v_T \]  \hspace{1cm} (7.10)

\[ M_T = 0.37 r_p F_T \]  \hspace{1cm} (7.11)

Combining Eqs. (7.8), (7.9), (7.10), and (7.11), we can calculate the critical tangential
velocity as:

\[ v_T^* = \frac{v_N r_b}{10.205 \sqrt{r_p^2 - r_b^2} + 3.776 r_p} \]  \hspace{1cm} (7.12)

Then, the probability of the particle straining is given by:

\[ P_{\text{straining}} = \exp \left( -\frac{v_T}{v_T^*} \right) \]  \hspace{1cm} (7.13)

When the particle size is smaller than the size of the selected bond, the particle
is able to enter that bond. Specially, if the selected bond has been fully packed, the particle is determined as packed within that bond. The probability of a particle reaching the bond wall was developed by Stein [207]:

\[
P_{\text{wall}} = 4 \left[ \left( \frac{r_p}{r_{be}} \right)^2 + \left( \frac{r_p}{r_{be}} \right)^3 + \left( \frac{r_p}{r_{be}} \right)^4 \right]
\] (7.14)

where \( r_{be} \) is the effective bond size, which we will discuss later. Once the particle arrives at the bond wall, particle trapping is possible depending on the torque balance test as shown by Figure 7.4(b):

\[
F_N \sqrt{r_p^2 - (r_p - h_b)^2} = F_T (r_p - h_b) + M_T
\] (7.15)

where \( h_b \) is the average height of the protrusions on the bond wall. Specially, \( F_N \) is the adhesive force between particle and bond wall. As reviewed by Oliveira [212], the adhesion is mainly caused by Van der Waals forces and electrostatic double-layer forces. In our current studies, we only took into account the Van der Waals forces which can be evaluated by:

\[
F_N = \frac{H r_p}{6 z_0^2}
\] (7.16)

where \( z_0 \) is the distance of closest approach, which is generally about 1 nm [280], \( H \) is the Hamaker constant which can be directly related to the dielectric constant \( \varepsilon_d \) and the index of refraction \( n_r \) of the species [281]. Combining Eqs. (7.10), (7.11), (7.15), and (7.16), we can determine the critical tangential velocity:

\[
v_r^* = \frac{H \sqrt{2 r_p h_b - h_b^2}}{6 z_0^2 \pi \mu \left[ 10.205 (r_p - h_b) + 3.776 r_p \right]}
\] (7.17)
Then, the probability of particle being trapped by the bond wall is estimated by:

\[ P_{\text{trapping}} = P_w \exp \left( -\frac{v_f}{v_T} \right) \]  \hspace{1cm} (7.18)

### 7.2.3 Network Permeability

As we inject more particles into the network, the hydraulic permeability on the network surface (cake filtration) and within the network structure (bond constriction) is changed. The laminar flow assumption was employed so that the pressure drop through the clean network bond could be described by the Hagen-Poiseuille equation:

\[ \Delta p_b = \frac{8\mu L_b}{r_b^2} \hat{J} \]  \hspace{1cm} (7.19)

where \( \hat{J} \) is the actual fluid velocity (flux) within the network bond. Therefore, the pressure distribution within the network can be determined by a mass balance at each node of the network.

#### 7.2.3.1 Network Boundary

The hydraulic resistance on the network surface caused by the particle cake layer is the combination of the resistance of the cake layer and the initial resistance between the particle and network. As derived in section 6.2.2, the resistance of the cake layer can be directly related to the particle size and the porosity of the cake layer. Therefore, we can get:

\[ R_{ns} = R_{c0} + n_{\text{packed}} \frac{24\pi (1 - \epsilon_c) r_p}{\epsilon_c^4 L_{ns} L_{sy}} \]  \hspace{1cm} (7.20)
where \( n_{\text{packed}} \) is the number of packed particles per site. Specially, when the particle covers more than one site \( (n_{\epsilon} > 1) \), only the site with complete blockage has the \( R_{e_0} \) term.

### 7.2.3.2 Network Bond

As discussed in section 7.2.2, there are three fouling cases (particle straining, particle trapping, and particle packing) within the network structure. The equations for evaluating the pressure drop caused by these fouling cases were summarized in Table 7.1. For a given network bond, the total pressure drop is the linear combination of the pressure drop of the clean network bond and the pressure drop caused by the captured particles:

\[
\Delta p_{bf} = \Delta p_b + \Delta p_{\text{straining}} + \Delta p_{\text{trapping}} + \Delta p_{\text{packing}}
\]  

Combining Eq. (7.21) and those equations for particles within the network in Table 7.1, we can evaluate the effective bond size \( r_{be} \) by:

\[
\frac{r_b^2}{r_{be}^2} = 1 + n_{\text{strained}} \frac{R_{e_0} r_p^2}{8L_b} + n_{\text{trapped}} \frac{3r_p}{L_b} \left[ 1 - \left( \frac{r_b - r_p}{r_b} \right)^2 \right] \left[ 1 + \frac{r_p}{r_b} \left( 2.104444 - 0.697 \left( \frac{r_b - r_p}{r_b} \right)^2 \right) \right] + n_{\text{packed}} \frac{3(1 - \epsilon_c) r_p}{\epsilon_e^2 L_b}
\]  

Therefore, the pressure drop of the fouled network bonds can be calculated based on the effective bond size:

\[
\Delta p_b = \frac{8\mu L_b}{r_{be}^2} \tilde{j}
\]
All computational procedures for the network-based fouling model were summarized in a flowsheet as shown by Figure 7.5.

7.3 Experimental Methods

7.3.1 Materials

Polystyrene microspheres with sizes of 0.25 \( \mu m \) and 0.54 \( \mu m \) were used as the foulant particles to verify the model predictions. The detailed information about the polystyrene microspheres and the method for preparing the feed solutions was introduced in section 3.2.2.

0.2 \( \mu m \) Anopore membrane (\( \epsilon_m = 0.6 \)), 0.2 \( \mu m \) PCTE membrane (GTTP, \( \epsilon_m \approx 0.15 \)), 0.1 \( \mu m \) PVDF membrane (VVLP, \( \epsilon_m = 0.7 \)), and 0.22 \( \mu m \) PVDF membrane (GVWP, \( \epsilon_m = 0.7 \)) were employed to perform the filtration experiments. The 0.2 \( \mu m \) Anopore membrane and 0.2 \( \mu m \) PCTE membrane have uniform straight-through cylindrical pores, while PVDF membranes have highly interconnected pores. Details about these filtration membranes were listed in Table 3.2.

7.3.2 Filtration Experiments

Both the 0.25 \( \mu m \) and 0.54 \( \mu m \) polystyrene microspheres with two concentration levels (0.000625 \( g/L \) and 0.0025 \( g/L \)) were filtered through 0.2 \( \mu m \) Anopore membranes to investigate the effects of particle size on the model predictions when external fouling is dominant. Then, a comparative study of two
membrane morphologies (straight-through pores and interconnected pores) was carried out by filtering 0.25 µm polystyrene microspheres (0.00125 g/L) through both the 0.1 µm PVDF membranes and the double-layer 0.2 µm PCTE membranes at 6 psi. Finally, the internal fouling mainly caused by the particle straining was simulated by filtering 0.25 µm polystyrene microspheres (0.00125 g/L) through the 0.22 µm PVDF membrane and the composite membrane with the 0.22 µm PVDF membrane on top of the 0.2 µm PCTE membrane. For comparison, the composite membrane with reversed orientation and the 0.2 µm PCTE membrane were also employed for repeating the same filtration experiments. The transmembrane pressure was 2 psi for the single layer membranes and 4 psi for the composite membranes. Details about the filtration experiments were introduced in section 3.3.1.

7.4 Results and Discussion

In this section, we examined the network-based fouling by comparing the model predictions with both the experimental results and the modeling results based on the conventional approaches. The program for the network-based fouling model is introduced in Appendix C.3. The parameters used for constructing the network for various membranes were listed in Table 7.2.

The bond size for both the 0.2 µm Anopore membrane and the 0.2 µm PCTE membrane are based on the membrane parameters listed in Table 3.2. As
revealed by Ghayeni [282], the porous PVDF membranes have a larger pore size than the nominal value. For example, the median pore size for the 0.22 \( \mu m \) PVDF membrane (both GVHP and GVWP) measured by the mercury intrusion method is 0.45 \( \mu m \). Therefore, the values of \( \bar{\tau}_b \) and \( \eta_b \) for the PVDF membranes were chosen so that the predicted membrane resistance gave reasonable agreement with the experimental results. The parameters for anisotropy (\( \varphi_r \) and \( \varphi_s \)) were set to 0.9 considering the compaction effects during the filtration.

Although we may get better simulation results by using more network sites, the number of network sites (\( n_{ex} \) and \( n_{ey} \)) was set to 50 considering our current computational ability. The bond length for the horizontal bonds was calculated based on Eq. (7.2). The number of network layers for the PVDF membranes was set to 100 so that the \( z \) bond length could be bounded to the order of magnitude of the maximum pore size. Less network layers were assigned to the PCTE and Anopore membranes due to the straight-through cylindrical pore structures.

### 7.4.1 External Fouling

As discussed in our earlier studies, the external fouling during the filtration was described by pore blockage and cake filtration, and the membrane morphology had significant impact on the fouling behavior. In following sections, we examined the network-based fouling model when external fouling is dominant.

#### 7.4.1.1 Pore Blockage and Cake Filtration

First, both the 0.25 \( \mu m \) and 0.54 \( \mu m \) polystyrene microsphere solutions
(0.000625 g/L and 0.0025 g/L) were filtered through 0.2 µm Anopore membranes at 2.5 psi. The experimental results were plotted as normalized flow rate versus filtration time as shown in Figure 7.6(a) for the 0.25 µm polystyrene microspheres and (b) for the 0.54 µm polystyrene microspheres. The blue curves are the model calculations based on the combined fouling model accounting for both pore blockage and cake filtration [75] with the parameters listed in Table 6.3. The red curves are the model calculations based on the network-based fouling model. The network structure parameters were listed in Table 7.2.

As discussed in section 6.4.2.1, the 0.54 µm polystyrene microspheres can cover more than one membrane pore \( n_s = 4 \) when filtering through the 0.2 µm Anopore membranes. The experimental value of \( R_{c0} \) for the 0.54 µm polystyrene microspheres is significantly lower than that for 0.25 µm polystyrene microspheres. We attributed this discrepancy to the fact that the covered membrane pores may not be completely blocked due to the spherical surface of the particles. In the network simulation, we verified this guess by employing the same \( R_{c0} \) for both the 0.25 µm and 0.54 µm polystyrene microspheres as we applied the spiral distribution rule for the case of \( n_{es} \) greater than one as discussed in section 7.2.2.1. For the case of the 0.25 µm polystyrene microspheres (Figure 7.6(a)), both model calculations are in good agreement with the experimental results. However, the network modeling yielded a slightly higher flux decline rate for the case of the 0.54 µm polystyrene microspheres as shown in Figure 7.6(b). We note that the number of covered sites \( n_{es} \) based on Eq. (7.7) is 5 while \( n_s \) predicted by Eq. (6.5) is 4. This
discrepancy is due to the minor deviation of the network structure from the actual membrane structure. Despite this deviation, the consistency between the network modeling and the experimental results indicates that the assumptions for surface blocking underlying the network model are valid. We also plotted the model calculations of the blocked area fraction versus filtration time in Figure 7.7. It shows that the modeling results based on the network approach (red curves) are consistent with those based on the combined fouling model (blue curves).

As a statistical approach, the network modeling can provide more insights regarding the fouling processes compared to the conventional fouling models which are mainly based on the continuum approach. In Figure 7.8, we demonstrated the evolution of the distribution of the captured particles on the network surface for 0.25 µm polystyrene microspheres filtering through the 0.2 µm Anopore membrane. The grayscale indicates the relative captured particle number per network surface area. The fraction of blocked area was varied from 0.1 to 0.99. It shows that the foulant particles were uniformly deposited on the network surface during the initial filtration as shown in Figure 7.8(a) and (b). As more particles were convected to the network surface, the heterogeneous cake layers were formed within the blocked regions (Figure 7.8(c) and (d)). However, the heterogeneity of the cake layer was minimized during the long time filtration due to the flow-biased probability as shown by (e) and (f). This is consistent with the prediction based on the combined fouling model that cake layer growth is a self-leveling process.

Figure 7.9 shows the evolution of the distribution of the captured particles on
the network surface for the 0.54 µm polystyrene microspheres filtered through the 0.2 µm Anopore membrane. The site clusters were yielded by the spiral distribution rule indicating more than one site was covered by a foulant particle \( n_{es} = 5 \). We also note that particle overlap occurred during the initial filtration as shown by Figure 7.9(a) and (b). This may not be true since such a packing is not stable when the fraction of blocked sites is still very low. Our current model is unable to account for the actual structure of the particle packing.

With the network modeling, we compared the completely blocked site distribution yielded by the 0.25 µm polystyrene microspheres with that yielded by the 0.54 µm polystyrene microspheres at the same blocked area fraction \( \theta = 0.9 \) as shown in Figure 7.10. It shows that less sites were completely blocked by the 0.54 µm polystyrene microspheres (Figure 7.10(b)) compared to the 0.25 µm polystyrene microspheres (Figure 7.10(a)). This comparative plot explains why the value of \( R_{c0} \) for the 0.54 µm polystyrene microspheres was lower than that for 0.25 µm polystyrene microspheres.

7.4.1.2 Membrane Morphology

The effects of the highly interconnected pore structures on the fouling behavior were successfully studied by the fouling model accounting for the membrane morphology [124]. Here, we compared this model with the modeling based on the network approach by applying these two models to the simulation of 0.25 µm polystyrene microspheres (0.00125 g/L) filtering through a double-layer 0.2 µm
PCTE membrane (straight-through pores) and 0.1 µm PVDF membrane (highly interconnected pores). We employed the stack of 0.1 µm PVDF membranes to minimize the difference of membrane resistance between the 0.1 µm PVDF membrane and a single layer 0.2 µm PCTE membrane.

The experimental results were plotted in Figure 7.11(a) as normalized flow rate versus filtration time. Blue curves are the model calculations based on the fouling model accounting for membrane morphology with the best fit parameters listed in Table 5.4. Red curves are the model calculations of the network modeling with the network structure parameters listed in Table 7.2. They show that both model predictions are in good agreement with the experimental results. The plots of the fraction of blocked area versus filtration time predicted by the modeling were displayed in Figure 7.11(b). We can see that the modeling results based on the continuum approach (blue curves) yielded a higher rate of pore blockage than that predicted by the network modeling (red curves) during the initial filtration. We also note that the curves predicted by the model accounting for the membrane morphology is slightly discontinuous at \( t = 47 \text{ min} \). This discontinuity is resulted from the shift from the central blockage model to the central void model as shown in Figure 1.6. This shift is necessary because the permeability ratio \( K \left( \frac{L_m}{r_{\text{blocked}}} \right)^2 \frac{k_r}{k_z} \), which was referred to as a constant in the modeling, is actually affected by the size of foulant aggregates \( r_{\text{blocked}} \). As the membrane is highly fouled, significant deviation will be yielded by the central blockage model since larger aggregates may be formed on the
membrane surface during the long time filtration. However, the point for shifting from central blockage to central void was chosen somewhat arbitrarily since the model is unable to predict the evolution of the particle distribution on the membrane surface. Here, we will show that the network modeling can account for this drawback of the continuum approach.

In Figure 7.12, we demonstrated the evolution of the clusters on the network surface for the 0.25 \( \mu m \) polystyrene microspheres (0.00125 g/L) filtering through the double-layer 0.2 \( \mu m \) PCTE membrane. A cluster of the blocked sites is defined as a set of connected blocked sites as indicated by the black regions in Figure 7.12. Inversely, the cluster of open sites is a set of connected open sites denoted by white regions. We can see that the clusters of blocked sites were scattered on the network surface during the initial filtration as shown by Figure 7.12(a). Clearly, this is consistent with the central blockage model. As more sites were blocked, the cluster size of the blocked sites was increased (Figure 7.12(b)), and the open region was gradually separated into many smaller clusters of open sites (Figure 7.12(c), (d) and (e)). When the network was highly fouled, the cluster size of blocked sites spanned the entire network unit, and the clusters of open sites were completely surrounded by the blocked sites (Figure 7.12(e)) as described by the central void model.

In contrast, the model calculations for the cluster distribution for the 0.25 \( \mu m \) polystyrene microspheres (0.00125 g/L) filtering through the 0.1 \( \mu m \) PVDF membrane was plotted in Figure 7.13. The similar evolution of the cluster distribution was observed indicating the smooth transition from the blocked site
dominant state (central blockage) to the open site dominant state (central void). We also note that larger clusters of blocked sites were yielded by the porous membrane (Figure 7.13(e)) compared to that given by straight-through membrane (Figure 7.12(e)) at the same filtration time \( t = 50 \text{ min} \). This is due to the fact that, for the membrane with highly interconnected pores, the open sites surrounding the clusters of blocked sites have a higher flow rate than that of the open sites far away from the blockage thereby providing a higher probability to capture the particles to form larger clusters.

In order to quantitatively demonstrate the evolution of the clusters, we also calculated the number of the clusters and the cluster size for the filtration with both the double-layer 0.2 \( \mu m \) PCTE membrane and the 0.1 \( \mu m \) PVDF membrane. In Figure 7.14(a), the number of blocked site clusters was plotted as a function of filtration time. A drastic increase of the blocked site clusters was demonstrated during the initial filtration, and a maximum was yielded at about 4 min. This maximum indicates the threshold of the combination of the blocked site clusters, which is similar to the threshold of the percolation as introduced in section 1.3.2.1. After reaching the maximum, the number of blocked site clusters was decreased with a relatively lower rate to one at about 40 min. We also note that 0.1 \( \mu m \) PVDF membrane had higher rate of number change compared to 0.2 \( \mu m \) PCTE membrane stack due to the higher flow rate yielded by the porous structures. In contrast, the number of open site clusters versus filtration time was plotted in Figure 7.14(b). It shows that the number of the open site clusters almost remained at one during the
initial filtration since most of the surface was dominated by the open sites. As the number of blocked site clusters began to decrease, the number of open site clusters increased gradually from one to a maximum at about 50 min. After that, the blocked area was increased primarily by reducing the clusters of open sites indicating the central void model.

The cluster size was represented by both the average number of the sites per cluster and the average span per cluster as shown in Figure 7.15. We can see that the size of blocked site clusters was increased as the size of open site clusters was reduced. The size of blocked site clusters spanned the entire network unit at about 40 min. All these studies indicate that the network modeling is able to account for the effects of the topology of blocked regions on the fouling behaviors, and the statistical results from the stochastic simulation are consistent with the predictions based on the conventional approaches.

7.4.2 Internal Fouling

As discussed in section 7.2.2.2, the internal fouling within the network structures was attributed to particle straining, particle trapping, and particle packing. These factors acting together affect the particle distribution within the membrane structure. Determining the particle distribution during the filtration time requires large-scale computations. For this reason, we proposed a method named single particle test (SPT) to examine the effects of the membrane properties on the particle distribution within the membrane structures.
In the single particle test, we injected one particle to the clean network. Following the computational procedures as developed in section 7.2.2.2, the final status of this particle can be determined. The same simulation was repeated thousands of times (>10000), and then, the individual computations were aggregated to get the particle distribution for the clean network. The network for the 0.22 \( \mu m \) PVDF membrane was employed as a template for all SPT calculations in this section.

As introduced in section 7.2.2.2, a torque balance test was employed for determining the probability of the particle straining. Here, we first investigated how this test affects the model predictions with SPT. The 0.25 \( \mu m \) microspheres were filtered through the network at 2 psi. In order to minimize the effects of particle trapping, the Hamaker constant \( H \) was set to zero indicating no adsorption. 20000 particles were injected for this SPT. The results of SPT were plotted in Figure 7.16(a) for the simulations without the torque balance test and (b) for the simulations with the torque balance test. It shows that the retention \( R_e \) for the 0.25 \( \mu m \) microspheres predicted by SPT without the torque balance is much higher (0.96) than that predicted by SPT with the torque balance (0.35). In Figure 7.16(a), we can see that most of particles were strained by horizontal bonds, and the upper network layers had higher probability than the lower layers. As the effects of the tangential flow on the strained particles were taken into account, most of the particles strained by horizontal bonds were released since the flow rate within the horizontal bonds was much lower than that within the \( z \) bonds. As a result, a relatively uniform distribution can be seen in Figure 7.16(b) for the simulation with the torque
balance.

**7.4.2.1 Theoretical Analysis with SPT**

First, we investigated the internal fouling caused by particle straining with SPT. $H$ was set to zero for eliminating the particle trapping. The effects of particle size, bond size distribution, and anisotropy of bond size were examined separately.

In the first system, SPT was performed with different sized microspheres. The size of the microspheres were varied from 0.1 to 0.4 $\mu m$. The results of SPT were demonstrated in Figure 7.17. We can see that the particle retention $R_p$ is significantly increased as larger particles are injected to the network. The probability of particle capture within the upper layers is increased as the particle size is closer to the average bond size. We also note that the probability of particle capture by horizontal bonds is slightly decreased for larger particles as shown by Figure 7.17(c). This is because the lever arm of tangential force acting on the strained particles is increased as indicated by Figure 7.4(a), thereby lower probability to capture the particles.

The bond size distribution is characterized by $\eta_b$, which is equal to the ratio of the standard deviation $\sigma_m$ to the average bond size $\bar{b}$. The lower $\eta_b$, the more uniform bonds a network has. In Figure 7.18, we demonstrated the results of SPT for 0.25 $\mu m$ microspheres with the network having different bond size distributions. When $\eta_b$ is equal to 0.4, almost all bond sizes are larger than the particle size as
shown by the Figure 7.18 (a). As a result, a relatively low retention (0.19) was yielded, and the particles were uniformly distributed through the entire profile. As $\eta_b$ was increased to 0.6, the portion of bonds with smaller size compared to the particle size was increased, thereby yielding higher particle retention (0.53) as displayed in Figure 7.18(b). For $\eta_b = 1$ (Figure 7.18(c)), it shows that most of the particles were rejected within the upper network layers due to the high retention (0.93).

The effects of anisotropy of bond size was investigated by SPT. $\varphi_r$, which is the average size ratio of horizontal bonds to $z$ bonds, was varied from 0.9 to 0.05 as demonstrated in Figure 7.19. When $\varphi_r$ is equal to 0.9 (Figure 7.19(a)), the size of the horizontal bonds is slightly smaller than that of the $z$ bonds, thereby implying a nearly equivalent probability of particle straining for both directions. In Figure 7.19(b), the value of $\varphi_r$ was decreased to 0.5 indicating a smaller bond size in the horizontal direction. It can be seen that the probability of particle straining by the horizontal bonds was significantly increased, and the total retention was also increased to 0.93. As a result, a nonuniform particle distribution was generated within the network, and most of particles were concentrated near the upper surface. It is interesting to note that the retention was decreased to 0.13 when a even smaller value of 0.05 was assigned to $\varphi_r$ as shown in Figure 7.19(c). This is because the lever arm of the normal force acting on the particles is almost equal to zero when the particle size is much larger than the bond size as indicated by Figure 7.4(a).

The particle trapping is primarily related to the adhesive forces between the
particles and bond walls. When the adhesive forces are dominated by the Van der Waals forces, the interaction between the particle and the bond wall is characterized by Hamaker constant $H$, which is on the order of $10^{-19}$ to $10^{-21}$ J [283]. In order to eliminate particle straining, $\eta_b$ was set to 0.3 so that the retention was decreased to 0.04 when $H$ is equal to zero. Then, the value of $H$ was varied from $1\times10^{-21}$ to $3\times10^{-21}$ J for examining the effects of the adhesive forces on the particle trapping. The SPT simulations were demonstrated in Figure 7.20. The graph clearly indicates that the particle trapping primarily occurs within the horizontal bonds due to the low tangential flow rate in the horizontal bonds. As the value of $H$ increased, the retention caused by the particle trapping almost linearly increased from 0.12 to 0.52.

We also employed SPT to investigate the effects of particle size on the particle trapping. The simulation results were plotted in Figure 7.21. As indicated in Figure 7.4(b), the lever arm of the tangential force acting on the particle will be decreased as the particle size decreases indicating a higher probability of trapping. However, Figure 7.21 shows that the retention caused by particle trapping was significantly decreased as the particle size was reduced from 0.25 to 0.025 \( \mu m \). This is because the probability of particle reaching the bond wall is related to the size ratio of particle to bond as shown by Eq. (7.14). As the probability of adsorption is increased, the smaller particles have less probability to arrive at the bond wall, and the net result is that the probability of trapping is decreased.
7.4.2.2 Model Validation

The modeling for internal fouling was validated by filtering 0.25 μm polystyrene microspheres (0.00125 g/L) through the 0.22 μm PVDF membrane (2 psi) and the membrane stacks of 0.2 μm PCTE membrane and 0.22 μm PVDF membrane (4 psi). The simulations were based on the structure parameters listed in Table 7.2. The estimated Hamaker constant for aqueous polystyrene microspheres based on PVDF is 2.30×10^{-21} J. Specially, the composite membranes composed of the 0.2 μm PCTE membrane and 0.22 μm PVDF membrane were simulated by setting ϕ, and ϕ, for the top layer (or the bottom layer for reversed arrangement) to zero since the thickness of the 0.22 μm PVDF membrane is much greater than that of 0.2 μm PCTE membrane as shown in Table 3.2.

The experimental data were compared with the results from network modeling in Figure 7.22. It shows that the model predictions are in good agreement with the experimental results. The single layer 0.2 μm PCTE membrane yielded the highest rate of flux decline as indicated by the solid squares. In contrast, the 0.22 μm PVDF membrane had a very low rate of flux decline denoted by void squares. It is interesting to note that the composite membrane with the 0.22 μm PVDF membrane on top of the 0.2 μm PCTE membrane had a higher flow rate during the initial filtration while a lower flow rate over the long time range compared to the reversed membrane arrangement. As concluded in CHAPTER 5, the composite membrane with highly interconnected pore structures in the top layer has the lower rate of flux decline than that of the composite membrane with
straight-through pore structure in the top layer when external fouling is dominant. Obviously, the experimental data from the composite membranes composed of 0.2 \( \mu m \) PCTE membrane and 0.22 \( \mu m \) PVDF membrane is contrary to this conclusion. This discrepancy indicates that internal fouling may dominate during the filtration with 0.22 \( \mu m \) PVDF membrane exposed to the feed stream. The conventional fouling models are unable to account for the evolution of internal fouling within the porous membrane structures.

With the network modeling, we employed the single particle test to examine the particle capture within the membrane structures. The results of SPT for the 0.25 \( \mu m \) polystyrene microspheres (0.00125 g/L) filtered through the composite membrane with the 0.22 \( \mu m \) PVDF membrane on top of the 0.2 \( \mu m \) PCTE membrane at 4 psi were demonstrated in Figure 7.23(a). Figure 7.23(a1) clearly shows that a large number of particles was able to flow through the 0.22 \( \mu m \) PVDF membrane, and arrive at the interface. Only a few of the particles were trapped by the network bonds, and uniformly distributed within the entire porous structures of the 0.22 \( \mu m \) PVDF membrane as shown by Figure 7.23(a2). In contrast, we plotted the particle distribution after 2 h of filtration (FTP) in Figure 7.23(b). The results of FTP are consistent with the results of SPT. We also note that more particles were trapped within the upper network layers during the filtration as indicated by Figure 7.23(b2). This is because the effective bond size was decreased during the filtration making the particles more likely to be trapped as indicated by Eq. (7.14). In Figure 7.23(b3), we can see that the particles were packed at the interface to form the internal
cake layer. This explains the lower flow rate for the composite membrane with 0.22 μm PVDF membrane on the top layer since thicker cake layer can be formed within the porous structures compared to the cake layer on the membrane surface.

7.5 Conclusions

In this study, a network-based fouling model was developed. The network modeling consists of three main elements: i) network construction; ii) particle flow; iii) permeability evaluation. A three-dimensional network was developed to simulate the homogeneous membranes with various morphologies. The particle capture on the network surface and inside the network was described by particle straining, particle trapping, and particle packing. The stochastic nature of the particle flow was taken into account by a series of rules based on probability tests. A mathematical model for estimating the effective bond size during the filtration was derived accounting for all fouling mechanisms. The network permeability was determined based on the effective bond size.

The network modeling was first compared with the combined fouling model accounting for both pore blockage and cake filtration. With the network approach, the evolution of the cake layer on the membrane surface was simulated for different sized particles. Then, the network-based fouling model was employed to simulate the membranes with straight-through pores and highly interconnected pores, and compared with the fouling model accounting for membrane morphology. A smooth
transition from the central blockage model to the central void model was successfully demonstrated by the network modeling. Finally, the single particle test based on the network modeling was applied to the theoretical analysis of the effects of membrane properties on internal fouling. The model predictions were validated by filtration experiments.

All these studies show that the network modeling is a useful tool to investigate the fouling behavior during the microfiltration. With the network-based fouling model, more information can be provided to help us get a deep insight into the fouling mechanisms.
### Table 7.1 Equations for Evaluating Pressure Drop of Fouled Network

<table>
<thead>
<tr>
<th>Straining</th>
<th>( \Delta p ) (Network Surface)</th>
<th>( \Delta p ) (Inside Network)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu R_{cb} \hat{J} )</td>
<td>( n_{strained \mu R_{cb} \hat{J}} )</td>
<td></td>
</tr>
<tr>
<td>Trapping</td>
<td></td>
<td>( n_{trapped} 24 \mu \frac{r_p}{r_b^2} \left[ 1 - \left( \frac{r_b - r_p}{r_b} \right)^2 \right] \left[ 1 + \frac{r_p}{r_b} \left[ 2.104444 - 0.697 \left( \frac{r_b - r_p}{r_b} \right)^2 \right] \right] \hat{J} ) [1]</td>
</tr>
<tr>
<td>Packing</td>
<td>( n_{packed} \frac{24 \pi (1 - \varepsilon_c) r_p}{\varepsilon_c^4 L_{dx} L_{dy}} \hat{J} )</td>
<td>( n_{packed} \frac{24 (1 - \varepsilon_c) r_p}{\varepsilon_c^4 r_b^2} \hat{J} )</td>
</tr>
</tbody>
</table>

[1]. Taken from Ref.[216].
### Table 7.2 Parameters for Constructing Networks

<table>
<thead>
<tr>
<th>$\bar{r}_b$ (µm)</th>
<th>$\eta_b$</th>
<th>$\varphi_r$</th>
<th>$\varphi_n$</th>
<th>$\varepsilon_{mx}$</th>
<th>$L_{nx}$ or $L_{by}$ (µm)</th>
<th>$n_{ex}$ or $n_{cy}$</th>
<th>$L_{bc}$ (µm)</th>
<th>$n_{xc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 µm PCTE</td>
<td>0.1</td>
<td>0.01</td>
<td>0</td>
<td>0.15</td>
<td>0.460</td>
<td>50</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>0.2 µm Anopore</td>
<td>0.1</td>
<td>0.01</td>
<td>0</td>
<td>0.6</td>
<td>0.229</td>
<td>50</td>
<td>30</td>
<td>3</td>
</tr>
<tr>
<td>0.1 µm PVDF</td>
<td>0.1</td>
<td>0.3</td>
<td>0.9</td>
<td>0.9</td>
<td>0.229</td>
<td>50</td>
<td>1.1</td>
<td>100</td>
</tr>
<tr>
<td>0.22 µm PVDF</td>
<td>0.225</td>
<td>0.5</td>
<td>0.9</td>
<td>0.9</td>
<td>0.631</td>
<td>50</td>
<td>1.2</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 7.1 Schematic diagram of three-dimensional network for simulation of membrane fouling.
Figure 7.2 Schematic diagram of determining the site cluster on the network surface when one particle is able to cover more than one network site.
Figure 7.3 Schematic diagram of fouling mechanism within the network structure
Figure 7.4 Schematic diagram of torque balance of particles within the network structures: a) particle straining b) particle trapping

\[ F_{rb} \geq F_{T} \sqrt{r_{p}^2 - r_{b}^2} + M_{T} \]

\[ F_{N} \sqrt{r_{p}^2 - (r_{p} - h_{b})^2} \geq F_{T} (r_{p} - h_{b}) + M_{T} \]
CHAPTER 7

Figure 7.5 Flowsheet for calculations of network-based fouling model

<table>
<thead>
<tr>
<th>Network Construction</th>
<th>Particle Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Network Layer</td>
<td>( n_{eq} )</td>
</tr>
<tr>
<td>Number of Network Site</td>
<td>( n_{ex} n_{ey} )</td>
</tr>
<tr>
<td>Bond Length</td>
<td>( L_{bx} L_{by} L_{bz} )</td>
</tr>
<tr>
<td>Bond Size</td>
<td>( \bar{r}_b )</td>
</tr>
<tr>
<td>Bond Size Distribution</td>
<td>( \eta_b )</td>
</tr>
<tr>
<td>Anisotropic Bond Size</td>
<td>( \phi_r )</td>
</tr>
<tr>
<td>Anisotropic Bond Density</td>
<td>( \phi_n )</td>
</tr>
</tbody>
</table>

Calculate effective bond size.  

\[ Q = ? \]

Generate a new particle  
Determine the entry of network by flow-biased probability.  
Has the entry been blocked?  
\( r_p > r_b ? \)

Reach a new node within the network.  
Pass the tests of both trajectory and torque balance?  
\( r_p > r_b ? \)

Pass the test of torque balance?  
Determine an exit by flow-biased probability.  
\( r_p > r_b ? \)

Surface Straining  
Surface Packing  
Internal Packing  
Internal Straining  
Trapping
Figure 7.6 Different sized polystyrene microspheres filtered through 0.2 µm Anopore membranes (2.5 psi): a) 0.25 µm PS beads; b) 0.54 µm PS beads. Blue solid curves are model calculations based on the combined fouling model accounting for both pore blockage and cake filtration (continuum approach), and red curves are model calculations based on the network-based fouling model (statistical approach).
Figure 7.7 Model calculations of the fraction of blocked area versus filtration time for PS beads (0.000625 g/L) with size of 0.25 \( \mu \)m and 0.54 \( \mu \)m filtered through 0.2 \( \mu \)m Anopore membranes at 2.5 psi.
Figure 7.8 Model calculations of foulant particle distribution on network surface for 0.25 µm PS beads filtered through a 0.2 µm Anopore membrane ($n_{ps}=1$). The grayscale indicates the relative particle numbers per network surface area.
Figure 7.9 Model calculations of foulant particle distribution on network surface for 0.54 $\mu$m PS beads filtered through a 0.2 $\mu$m Anopore membrane ($n_{eq}=5$). The grayscale indicates the relative particle numbers per network surface area.
Figure 7.10 Completely blocked sites on network surface ($\theta=0.9$) for a) 0.25 $\mu$m PS beads and b) 0.54 PS beads filtered through 0.2 $\mu$m Anopore membranes.
Figure 7.11 0.25 μm PS beads (0.00125 g/L) filtered through a double-layer 0.2 μm PCTE and a 0.1 μm PVDF membranes (6 psi): a) normalized flow rate versus filtration time; b) model calculations of fraction of blocked area versus filtration time. Blue solid curves are model calculations based on the fouling model accounting for membrane morphology (continuum approach), and red solid curves are model calculations based on the network-based fouling model (statistical approach).
Figure 7.12 Distribution of clusters of blocked sites (black sites) and open sites (white sites) on network surface for 0.25 μm PS beads (0.00125 g/L) filtered through a double-layer 0.2 μm PCTE membrane at 6 psi.
Figure 7.13 Distribution of clusters of blocked sites (black sites) and open sites (white sites) on network surface for 0.25 µm PS beads (0.00125 g/L) filtered through a 0.1 µm PVDF membrane at 6 psi.
Figure 7.14 Number of clusters on network surface ($n_{ex}=n_{ey}=50$) versus filtration time for 0.25 $\mu$m PS beads (0.00125 g/L) filtered through a double-layer 0.2 $\mu$m PCTE membrane and a 0.1 $\mu$m PVDF membrane (6 psi): a) cluster of blocked sites; b) cluster of open sites.
Figure 7.15 Average cluster size, 1) number of sites per cluster, 2) and 3) site span per cluster, versus filtration time for 0.25 µm PS beads (0.00125 g/L) filtered through a double-layer 0.2 µm PCTE membrane and a 0.1 µm PVDF membrane (6 psi): a) cluster of blocked sites; b) cluster of open sites.
Figure 7.16 SPT ($n_p=20000$) for 0.25 µm microspheres filtered through the network with the structure parameters (Table 7.2) for 0.22 µm PVDF (H=0): a) without torque balance for particle straining; b) with torque balance for particle straining.
Figure 7.17 SPT ($n_b=20000$) for microspheres with different size filtered through the network with the structure parameters (Table 7.2) for 0.22 $\mu$m PVDF ($\eta_b=0.55$, $H=0$): a) $\Phi_p=0.1 \mu m$; b) $\Phi_p=0.25 \mu m$; c) $\Phi_p=0.4 \mu m$. 

![Figure 7.17](image-url)
Figure 7.18 SPT ($n_p=20000$) for 0.25 µm microspheres filtered through the network with the structure parameters (Table 7.2) for 0.22 µm PVDF (H=0): a) $\eta_b=0.4$; b) $\eta_b=0.6$; c) $\eta_b=1.0$. 

$\eta_b = 0.40$
$R_e = 0.19$

$\eta_b = 0.60$
$R_e = 0.53$

$\eta_b = 1.00$
$R_e = 0.93$
Figure 7.19 SPT ($n_p=20000$) for 0.25 $\mu$m microspheres filtered through the network with the structure parameters (Table 7.2) for 0.22 $\mu$m PVDF (H=0): a) $\phi_r=0.90$; b) $\phi_r=0.50$; c) $\phi_r=0.05$. 
Figure 7.20 SPT ($n_p=20000$) for 0.25 µm microspheres filtered through the network with the structure parameters (Table 7.2) for 0.22 µm PVDF ($\eta_b=0.3$): a) $H=1 \times 10^{-21}$; b) $H=2 \times 10^{-21}$; c) $H=3 \times 10^{-21}$. 
Figure 7.21 SPT ($n_p=20000$) for microspheres with different size filtered through the network with the structure parameters (Table 7.2) for 0.22 $\mu$m PVDF ($\eta_b=0.3$): a) $\Phi_p=0.25$ $\mu$m; b) $\Phi_p=0.125$ $\mu$m; c) $\Phi_p=0.025$ $\mu$m.
Figure 7.22 0.25 µm PS beads (0.00125 g/L) filtered through the composite membrane composed of 0.2 µm PCTE and 0.22 µm PVDF membranes. Solid curves are model calculations based on the network structure parameters in Table 7.2.
Figure 7.23 0.25 µm PS beads (0.00125 g/L) filtered through the composite membranes with 0.22 µm PVDF membrane on top of 0.2 µm PCTE membrane at 4psi: a) SPT ($n_b=20000$); b) FPT ($t=2$ h).
CHAPTER 8 A Network-Based Fouling Model: II. Optimizing Asymmetry of Microfiltration Membranes

8.1 Introduction

As discussed in section 5.1, asymmetric membranes have better performance compared to symmetric or homogeneous membranes. However, more complex fouling behavior was observed during the filtration with asymmetric membranes, especially when both external fouling and internal fouling are important.

For example, Zhang et al. [284] investigated the filtration of ethanol fermentation medium, which contained both glucose and yeast cells, with both symmetric and asymmetric membranes. It was found that the asymmetric membrane had a lower flux decline rate compared to the symmetric membrane as the concentration of glucose increased, while more serous fouling was observed for the asymmetric membrane with various yeast cell concentrations. The virus filtration membranes, which have a very thin skin layer on top of a porous substrate layer, are typically used with the skin layer facing the feed stream for tangential flow filtration (TFF). However, some studies [15, 137] revealed that the reversed membrane orientation, i.e., having the membrane with the porous substrate layer exposed to the feed stream, yielded significantly greater capacity when the operation mode is normal flow filtration (NFF). The mitigation of the flux decay was attributed to the porous substrate layer within which the foulant aggregates could be captured thereby
protecting the skin layer.

In CHAPTER 5, we extended the fouling model accounting for the membrane morphology developed by Ho and Zydney [124] to accommodate the asymmetric membrane structures by varying both the permeabilities in the horizontal and transverse direction along the membrane profile. However, both the original model and the extended model are unable to predict the permeability profiles when internal fouling occurs.

As shown in CHAPTER 7, the modeling based on the network approach was able to predict the evolution of the foulant particle distribution within the membrane structure. It indicates that the network approach has the potential to account for the effects of asymmetric membrane structure on the fouling behavior as the network for a homogeneous membrane can be modified to accommodate asymmetry. Jackson et al. [229] employed the Voronoi tessellation to simulate the homogeneous porous media, and then modeled the composite membranes by using a combination of these networks. In the studies by Baralla et al. [285], a computer model based on a two-dimensional Voronoi tessellation was proposed to represent the porous structure of an asymmetric inorganic membrane and to simulate the fouling process. However, the coordinate number for this asymmetric network was only 3, and it is difficult to vary the asymmetric profile due to the complexity of the network construction.

The objective of this study was to modify the network-based fouling model developed in CHAPTER 7 to account for the effects of the asymmetric membrane structures on the fouling behavior. A mathematical approximation was proposed to
characterize the asymmetry of the membrane properties thereby generating the asymmetric networks based on the assumption of bond combination. Then, the model predictions were validated by filtering different sized polystyrene microspheres through two distinct asymmetric membranes: a PPVG membrane (uniform substrate layer) and a VP membrane (substrate layer with gradient pores). This modified network-based fouling model can provide deep insight regarding the different fouling mechanisms during the filtration with the asymmetric membranes, and is a very useful tool to optimize the asymmetry of the microfiltration membranes for better fouling resistance.

8.2 Theory

The network-based fouling model for symmetric membranes has been introduced in CHAPTER 7. In order to extend this model to account for the asymmetric membrane structures, we modified the rules for constructing the network while keeping those rules for particle flow and permeability evaluation the same for the current studies.

8.2.1 Network Accounting For Asymmetry

For an asymmetric membrane, not only the membrane pore size but also the other membrane properties, like pore density, pore connectivity, and so on, may vary along the membrane profile. The variation of pore size can be easily accounted for by varying the average bond size $\bar{r}_b$ for each network layer. However, as indicated by Eq. (7.2), the variation of pore density (the number of membrane pores per unit
membrane area) may significantly affect the length of both the \(x\) and \(y\) bonds when the membrane is highly asymmetrical.

If the membrane area represented by the network is fixed, more network bonds are needed within the network layers with higher pore density thereby requiring more computational effort. For example, the virus filtration membrane PPVG (Table 3.2) has a skin layer with a pore density almost 60 times higher than that of the substrate layer. In order to account for the variation of the pore density while avoiding large-scale computation, we combined the bonds within the network layers with higher pore density. Therefore, the number of subbonds per bond combination \(n_{sb}\) is determined based on the pore density:

\[
n_{sb} = \text{round} \left( \frac{L_{nx} L_{ny} \varepsilon_{ms}}{\pi \bar{r}_b} \right) \quad (8.1)
\]

Here, \(\varepsilon_{ms}\) is the fraction of pore area per unit area of membrane cross-section, and both \(\varepsilon_{ms}\) and \(\bar{r}_b\) are functions of the depth of the asymmetric membrane. Specially, \(n_{sb}\) within the layer with the lowest pore density is usually bounded to be 1 so that the total membrane area represented by the network could be maximized.

The bond combinations are schematically shown in Figure 8.1. The lines in the network represent the bond combination, and number of subbonds per bond combination is indicated by different colors. Blue denotes the bond combination with lower \(n_{sb}\), while red denotes the bond combination with higher \(n_{sb}\). In contrast to the network for the symmetric membranes as shown in Figure 7.1, the network for asymmetric membranes keeps the same geometrical configuration, i.e.,
the number of bonds (bond combinations) and the number of nodes, thereby requiring
the equivalent computational effort. Implicitly, we assumed that the subbonds within
a given bond combination share the same bond size which gives rise to the same
pressure drop.

8.2.2 Mathematical Approximation for Asymmetric Profile

The variation of the membrane properties along the membrane profile can be
directly determined by experimental measurements. However, it is much easier for
us to design or optimize the asymmetric structures if the asymmetric profile could be
approximated by a mathematical model with adjustable parameters.

In the current studies, we are focused on asymmetric membranes with a
monotonic profile. Therefore, we can describe the variation of the membrane
properties by using a power function:

\[
\frac{f_m(z^*)}{f_m(0)} = (1 - \eta) \left(1 - z^*\right)^N + \eta
\]  

(8.2)

where \( f_m(z^*) \) represents the dependent membrane properties, like pore size, surface
porosity, and so on, and \( z^* \) is the normalized position of the membrane \( \frac{z}{L_m} \).

There are two parameters in Eq. (8.2), \( \eta \) and \( N \). \( \eta \) is defined as the ratio of the
membrane property in the bottom layer to that in the top layer:

\[
\eta = \frac{f_m(1)}{f_m(0)}
\]  

(8.3)

When \( \eta \) is greater than one, the value of a given membrane property is
monotonically increased; for \( \eta \) less than one, it gives rise to a monotonically decreasing profile. Specially, the symmetric structures are yielded as \( \eta \) is equal to one.

The exponent \( N \) in Eq. (8.2) governs the rate of change of \( f_m \) with varying \( z^* \), thereby yielding various asymmetric profiles. The plot of \( f_m \) versus \( z^* \) based on Eq. (8.2) was displayed in Figure 8.2(a) for \( \eta > 1 \) and (b) for \( \eta < 1 \). It shows that \( f_m \) varies linearly from the top of the membrane to the bottom when \( N \) is equal to one. If the value of \( N \) is greater than one, for the case of \( \eta > 1 \), \( f_m \) varies with a concave down profile. As the value of \( N \) increases, the change of \( f_m \) is concentrated in a narrower region next to the membrane surface. If \( f_m \) represents the membrane pore size \( r_m \), the pore size profile of PPVG membrane, which has a very thin layer with smaller pore size (Figure 3.3(a)), can be approximated by the curve generated by \( N = 50 \ (\eta > 1) \) as shown in Figure 8.2(a). Inversely, a concave up profile is yielded by \( N \) less than one when \( \eta \) is greater than one. This case indicates a relatively slow change near the membrane surface compared to the sharp increase near the bottom. It is interesting to note that the curve for \( N = 0.5 \) (Figure 8.2(a)) is similar to the pore size profile of the VP membrane as shown by the SEM images in Figure 3.3(b). For the case of \( \eta < 1 \) as shown in Figure 8.2(b), an inverse tendency is yielded by the same value of \( N \), i.e., concave up profiles for \( N > 1 \) and concave down curves for \( N < 1 \). These profiles can be used to simulate the cases for the asymmetric membranes with reversed orientation.
8.3 Experimental Methods

8.3.1 Materials

In order to examine the effects of the relative size of foulant particles compared to the membrane pore size, three polystyrene microspheres with sizes of 0.053 \( \mu m \), 0.14 \( \mu m \) and 1.01 \( \mu m \) were employed in the current studies. The detailed information about the polystyrene microspheres and the method for preparing the feed solutions were introduced in section 3.2.2.

Two asymmetric membranes with different substructures in the substrate layer were used to study the effects of the asymmetric structures on the fouling behavior. They are a PPVG membrane with a uniform substrate layer and a VP membrane with a graded pore substrate layer. Details about these two asymmetric membranes were listed in Table 3.2.

8.3.2 Filtration Experiments

Different sized polystyrene microspheres (0.053 \( \mu m \), 0.14 \( \mu m \) and 1.01 \( \mu m \)) were filtered through both PPVG and VP membranes. The transmembrane pressure was 10 psi for the PPVG membranes and 12 psi for the VP membranes to yield an initial flux around \( 1.5 \times 10^{-4} m/s \). The filtration experiments were first performed with the skin layer facing the feed solution, and then repeated for the reversed orientations. The solution concentration for the 0.053 \( \mu m \) polystyrene
microspheres was 0.00025 g/L, and increased to 0.0005 g/L and 0.005 g/L for the 0.14 μm and 1.01 μm polystyrene microspheres, respectively. Details about the filtration experiments were introduced in section 3.3.1.

8.3.3 Membrane Characterization

Scanning electron microscopy was used to characterize the asymmetric membranes fouled by different sized polystyrene microspheres. Both the cake layer surface and the cross-section of the PPVG membranes fouled by the 1.01 μm polystyrene microspheres (0.00125 g/L, 10 psi, 2 h) were imaged by SEM following the procedures introduced in section 3.3.2.1. Both the PPVG (10 psi) and VP (12 psi) membranes were fouled by 0.14 μm and 1.01 μm polystyrene microspheres with the substrate layer exposed to the feed solutions (0.002 g/L, 2 h). The fouled membrane samples were sent to Millipore (Bedford, MA, USA), and SEM images were taken at different depths of the membrane cross-section by Christina Bondy.

8.4 Results and Discussion

In this section, first, we theoretically analyzed the effects of the asymmetric membrane structures on the normalized flow rate with the fouling model accounting for membrane morphology. Then, the network-based fouling model was applied to the simulation of the filtration with both the PPVG and VP membranes.
8.4.1 Theoretical Analysis

Although network modeling is able to provide more details about the fouling behaviors as shown in CHAPTER 7, more computational efforts are required compared to the conventional approaches. In CHAPTER 5, the fouling model accounting for the membrane morphology was extended to accommodate the asymmetric structures by varying the hydraulic permeability along the membrane profile. It is interesting to note that both models are based on the principle of conservation. However, the network modeling can cope with a more complicated boundary while a simplified boundary is required for the conventional methods, which usually employ a PDE to describe the fluid field. Despite this shortcoming, the fouling model accounting for the membrane morphology is a useful tool to investigate the fouling mechanisms. Here, we combined this model with the mathematical approximation of the asymmetric profiles as developed in section 8.2.2 to theoretically analyze the effects of the continuous asymmetric membrane profiles on the fouling. This will help us to get a better understanding as we discuss the network modeling in the following section.

8.4.1.1 Effects of Asymmetric Profile

As mentioned in section 8.2.2, the variation of \( f_m \) is characterized by \( N \). When the asymmetric membranes have a porous structure \( (K=1) \), the asymmetry is dominated by the variation of pore size and pore density, which are directly related to the hydraulic permeability in the transverse direction \( k_z \). For this reason, we
specified $f_m$ with $k_z$, and the asymmetric profiles of $K_z$ can be generated by varying the value of $N$ based on Eq. (8.2). The value of $\eta$ for $k_z$ was set to 100 indicating the membrane with tighter structure in the upper surface. We also reversed this asymmetric membrane by setting $\eta$ to 0.01. In addition, we assumed that the impermeable foulant layer is located on the membrane surface with $\theta$ equal to 0.64 (central blockage). Therefore, the normalized flow rate can be evaluated by the model developed in section 5.2 as varying $N$ from 0.1 to 100.

The model calculations for the asymmetric membranes with both orientations ($\eta=100$ and $\eta=0.01$) were plotted in Figure 8.3. According to this plot, the normalized flow rate for the membrane with a tight surface ($\eta=100$) was slightly decreased to a minimum as the value of $N$ increased from 0.1 to 1. Over the region of $N<1$, the change of $k_z$ is concentrated in the layer near the bottom. As the value of $N$ increased, the average resistance of the lower layer is reduced thereby decreasing the normalized flow rate. When it comes to the case of $N>1$, increasing $N$ will move the region with higher gradient of $k_z$ to the layer near the upper surface indicating higher resistance within the lower layer. As a result, an increase of the normalized flow rate can be seen as $N$ increases from 1 to 100. The calculation results for the membrane with the reversed orientation ($\eta=0.01$) demonstrated an inverse curve with a maximum at $N=1$.

The flow streamlines within the asymmetric structures were plotted in Figure 8.4 and Figure 8.5 for $\eta=100$ and $\eta=0.01$, respectively. When $N$ is equal to 0.1 for $\eta=100$ (Figure 8.4 (a)), a very thin layer with higher permeability was
yielded at the bottom surface. This thin layer had little impact on the lateral flow as
compared to the results for the homogeneous membranes in Figure 5.4(b2). The
linear asymmetric profile increases the permeability within the lower layer compared
to the case of \( N = 0.1 \). Therefore, the fluid flow was distributed into the blocked
region within a lower layer as shown in Figure 8.4 (b). When \( N \) is much greater
than one, most of the membrane resistance is concentrated within a very thin layer
near the upper surface as shown by the left panel in Figure 8.4 (c). As a result, the
fluid can flow farther in the radial direction within the upper layer.

As the asymmetric membranes were reversed (\( \eta = 0.01 \)), the variation of \( N \)
had little impact on the flow streamlines as shown by Figure 8.5. The normalized
flow rate is significantly higher than that of the membrane with a tight top layer.
This is consistent with the conclusions in CHAPTER 5.

8.4.1.2 Effects of Foulant Distribution within Membrane Structures

Although the fouling model accounting for the membrane morphology is
unable to predict the permeability profiles during the filtration when internal fouling
occurs, the internal blockage can be approximated by a very thin (\( \frac{\Delta z}{L_m} \ll 1 \))
impermeable foulant layer within the membrane structures as shown in the studies of
Ho [286]. Here, we employed this procedure to study the effects of the foulant
distribution within the asymmetric structures.

In most cases, the internal fouling occurs when the more open side of the
membrane is facing the feed stream. For this reason, the permeability $k_z$ ratio of the bottom to the top was set to 0.01 indicating higher hydraulic resistance in the lower layer. Three asymmetric profiles of $K_z$ were investigated by setting $N$ to 0.1, 1, and 10. The normalized depth of the impermeable foulant layer was varied from 0 to 0.95, and the fraction of the blocked area was 0.64 (central blockage). The simulations were performed with the model developed in section 5.2, and the calculation results were plotted in Figure 8.6 as normalized flow rate versus the normalized depth of impermeable foulant layer.

In Figure 8.6, the blue curve represents the asymmetric membrane which has a thin layer with lower resistance in the upper surface ($N = 0.1$). It shows that the normalized flow rate almost linearly decreased as the impermeable foulant layer moved from the upper surface to the bottom. For a linear asymmetric profile ($N = 1$), a slower decline can be seen as indicated by the black curve in Figure 8.6. In contrast, the plot for the asymmetric membrane with a thin tight layer in the bottom ($N = 10$) demonstrated a dramatic decline as indicated by the red curve in Figure 8.6. It shows that the normalized flow rate was significantly decreased as the impermeable foulant layer moved from 0 to 0.3. After that point, the normalized flow rate remained nearly unchanged over the region between 0.3 and 0.7. As the depth of the foulant layer increased beyond the 0.7, significant decline was observed again.

The flow streamlines within the asymmetric structures were plotted in Figure 8.7 and Figure 8.8 for $N = 0.1$ and $N = 10$, respectively. In Figure 8.7, we can see that the distance of the lateral flow into the blocked area was reduced as the depth of
the impermeable foulant layer increased. For the case of $N = 0.1$, most of the lower layer (from 0.1 to 1) has a higher resistance compared to the thin layer near the upper surface. As a result, shortening the span of the lateral flow significantly decreased the normalized flow rate. When $N$ is equal to 10, the layer with higher resistance is narrowed to a very thin region next to the bottom surface. It indicates that most of the membrane has a relatively low resistance. For this reason, although the similar flow streamlines were observed for the case of $N = 10$ (Figure 8.8), the normalized flow rate declined with a lower rate as the impermeable foulant layer moved from 0.1 to 0.9.

8.4.2 Model Validation

In current study, two asymmetric membranes were employed to validate the network modeling: i) a PPVG membrane, which has a very thin skin layer on top of a uniform porous substrate layer; ii) a VP membrane, which has a graded pore structure. Different sized polystyrene microspheres were filtered through both membranes. The microsphere size was chosen based on the average pore size of the substrate layer so that different fouling mechanisms may dominate as the particle size changed. All filtration experiments were performed with two membrane orientations: i) skin layer exposed to the feed stream; ii) substrate layer exposed to the feed stream.

The parameters for constructing the asymmetric networks were listed in Table 8.1. These parameters were chosen based on both the membrane properties listed in Table 3.2 and the SEM images shown in Figure 3.3. The bond length of the
horizontal bonds was determined by the parameters for the bottom layers with Eq. (7.2) so that the number of subbonds per bond combination within the substrate layer was bounded to be order one. The distance of closest approach $z_0$ was set to $5 \times 10^{-9}$ m, and Hamaker constant $H$ was estimated by the Lifshitz theory, which relates $H$ to the dielectric constant $\varepsilon_d$ (PVDF 9.0 [287], PES 3.5 [288], PS 2.5 [289], Water 78.4 [290]) and the index of refraction $n_r$ (PVDF 1.42 [175], PES 1.65 [291], PS 1.58, Water 0.8 [175]). The calculated $H$ for aqueous polystyrene microspheres is $2.30 \times 10^{-21}$ J based on PVDF or $2.65 \times 10^{-21}$ J based on PES. The roughness of the asymmetric membrane ($\frac{h_b}{r_b}$) was unknown. The choice of the value for this ratio was somewhat arbitrary, but it should be in the order of magnitude 0.001 in terms of the SEM images. The program for the network modeling was introduced in Appendix C.3.

### 8.4.2.1 Foulant Particles with Large Size

In the first system, 1.01 $\mu$m polystyrene microspheres (0.005 g/L), whose size is larger than the pore size of both the substrate layer and skin layer, were filtered through both PPVG (10 psi) and VP (12 psi) membranes with the skin layer up and substrate layer up. It was expected that the external fouling was dominant for all filtrations. The experimental data were plotted as normalized flow rate versus filtration time and particle loading in Figure 8.9(a) and (b), respectively. The solid curves are network modeling based on the parameters listed in Table 8.1. The model predictions are consistent with the experimental results.
According to the plot in Figure 8.9, the asymmetric membranes with the skin layer facing the feed stream had a higher flux decline rate compared to the reversed orientation. This is consistent with the theoretical analysis in section 8.4.1.1. We also note that, for the same orientation, the VP membranes (solid triangles) yielded a relatively low flux decay compared to the PPVG membranes (solid squares). As predicted in section 8.4.1.1, for the membranes with the tight layer facing the feed stream, the asymmetric profile with $N = 10$ (PPVG) has a slightly higher normalized flow rate than that of the profile with $N = 0.5$ (VP) as shown by Figure 8.3. This discrepancy is due to the fact that the resistance of the VP membrane ($4.8 \times 10^{11} \text{ m}^{-1}$) is greater than that of the PPVG membrane ($3.9 \times 10^{11} \text{ m}^{-1}$) thereby decreasing the relative resistance of the cake layer.

The network modeling yielded lower flux decay during the initial filtration compared to the experimental data. This is likely due to the fact that the realistic particle packing on the membrane surface has less particle overlap than that predicted by the modeling under the condition of low fraction of blocked area as discussed in section 7.4.1.1. During the long time filtration, the discrepancy between the modeling and the experiment may be attributed to the deviation of the estimation for the resistance of cake layer or the initial resistance of a single particle.

The membrane samples of the PPVG fouled by the 1.01 $\mu m$ polystyrene microspheres ($0.00125 \text{ g/L, } 2 \text{ h}$) were imaged by SEM as shown in Figure 8.10(a) for the skin layer up and (b) for the substrate layer up. The assumption of external fouling was verified by the images of the cross-section (Figure 8.10(a1) and (b1))
indicating all the 1.01 $\mu m$ polystyrene microspheres were rejected by the upper surface for both orientations. According to the upper surface images, relatively loose particle packing was yielded by the membrane with the substrate layer up (Figure 8.10(b2)) compared to that by the membrane with the skin layer up (Figure 8.10(a2)) due to the rough surface of the open side.

8.4.2.2 Foulant Particles with Medium Size

In the second system, we chose 0.14 $\mu m$ polystyrene microspheres (0.0005 g/L) as the foulant particle to test the asymmetric membranes. For both the PPVG and VP membranes, the particle size of the 0.14 $\mu m$ polystyrene microspheres is smaller than the average pore size of the substrate layer while it is still significantly greater than the average pore size in the tight layer. Therefore, it was expected that internal fouling may occur when the substrate layer is exposed to the feed stream while external fouling still dominates for the case of the skin layer up. Lower solution concentration was applied for three reasons: i) to highlight the fouling behaviors during the initial filtration; ii) to minimize the difference of the cake layer resistance caused by the change of particle size; iii) to mitigate the large-scale computations for network modeling.

The experimental results (scatter plot) were compared with the network modeling (line plot) in Figure 8.11. It clearly shows that the model predictions are in agreement with the experimental data. For PPVG membranes, the filtration with the substrate layer facing the feed stream yielded higher rate of flux decline compared to
the reversed arrangement. This is consistent with the theoretical analysis in section 8.4.1.2 which predicted that the internal foulant layer could decrease the normalized flow rate. However, a contrary result was observed for the filtration with the VP membranes. It can be seen in Figure 8.11 that the normalized flow rate of the VP membrane with the substrate layer up was significantly higher than that of the reversed membrane. This discrepancy indicates that the substructures of the substrate layer may have impact on the particle distribution.

With the network modeling, we were able to track each particle injected into the network during the filtration. Therefore, the particle capture rate (\( CR \)) indicating the number of captured particles per minute can be calculated for each network layer. For the case of 0.14 \( \mu m \) polystyrene microspheres filtering through PPVG with substrate layer up, the particle capture rate of each network layer was plotted as a function of filtration time in Figure 8.12(a) for particle straining, (b) for particle trapping, and (c) for particle packing. The grayscale indicates the relative capture rate (\( \frac{CR}{CR_{\text{max}}} \)), and the value of \( CR_{\text{max}} \) was listed in each panel in Figure 8.12. It clearly shows that the particle straining was dominant for both the horizontal bonds (upper panel) and \( z \) bonds (lower panel). We also note that the particle straining primarily occurred at the network layers near the skin layer (bottom), and the capture rate was slightly decreased during the long time filtration. The capture rate of trapping was much lower than that of particle straining. According to Figure 8.12(b), the particle trapping occurred primarily within the upper layers during the long time
filtration. This is because this is proportional to the bond size. As we fixed the value of \( \frac{h_b}{r_b} \), the height of the protrusions within the upper layers with larger bond size is greater than that within the lower layers with smaller bond size resulting in a higher probability of particle trapping. The lower flow rate during the long time filtration also reduced the tangential forces acting on the particles. As most of the bonds at the skin-substrate interface were blocked, the particles were packed within those blocked regions as indicated by Figure 8.12(c).

In contrast, the capture rate calculations for the VP membrane with the substrate layer up were plotted in Figure 8.13. Similar to that for PPVG membrane shown by Figure 8.12, the maximum capture rate of particle straining was much greater than that of particle trapping and packing indicating the dominant pore blockage within the membrane structures. The most interesting thing is that the particle straining occurred within the network layers far away from the skin-substrate interface, and the strained particles were distributed to a broader region in the transverse direction as indicated by Figure 8.13(a). This can explain why the VP membrane with the substrate layer up yielded a lower flux decline compared to the reversed arrangement. According to Figure 8.13(b), particles were uniformly trapped by the horizontal bonds within the upper network layers while the particle trapping by \( z \) bonds was concentrated within the layers blocked by particles. Both regions had a relatively low flow rate compared to the other regions thereby corresponding to a higher probability to trap the particles. We also note that more
particles were packed within the blocked network layers as indicated by Figure 8.13(c) compared to that of the PPVG membrane (Figure 8.12(c)). This is because the bond combinations within the upper network layers have less subbonds than the bond combinations within the lower network layers thereby requiring more particles to completely block that region.

We also compared the results of the SPT with the calculated particle distribution after the filtration (FTP). The calculation results for the PPVG membrane with the substrate layer up were plotted in Figure 8.14. It shows that the results of FTP are similar to the results of SPT. Both results indicate that the particle straining was concentrated at the region near the skin-substrate interface, and the trapped particles had a relatively uniform distribution along the network layers. Figure 8.15 shows the comparative plot of SPT and FTP for the VP membrane with the substrate layer up. The FTP for particle straining is consistent with the results of SPT as indicated by Figure 8.15(a). It is interesting to note that more particles were trapped by \( z \) bonds due to the decrease of effective bond size during the filtration compared to the results predicted by SPT (Figure 8.15(b)). There was no particle packing in SPT since the simulation was based on the clean network.

The effective bond size directly reflects the change of the network permeability. Therefore, we demonstrated the effective bond size as a function of filtration time for each network layer in Figure 8.16(a) for the PPVG membrane and (b) for the VP membrane. The grayscale indicates the value of the squared ratio of effective bond size to original bond size. It clearly shows that the reduction of
network permeability was primarily attributed to the $z$ bonds.

In order to verify the these predictions by network modeling, both the PPVG and VP membranes were fouled by 0.14 $\mu m$ polystyrene microspheres (0.002 g/L, 2 h) with the substrate layer facing the feed stream, and the cross-section of the fouled membrane was observed by SEM. The SEM images for the PPVG membrane samples were demonstrated in Figure 8.17. The images were taken from different positions within the cross-section. The left panel is the whole cross-section with a white box around the area for high magnification images in the right panel. It clearly shows that most of particles were deposited within the porous structures near the skin-substrate interface indicated by Figure 8.17(c) while few particles could be found within the upper structures (Figure 8.17(a) and (b)). In contrast, the SEM images for the VP membrane samples were displayed in Figure 8.18. It can be seen that more particles were found within the upper structures (Figure 8.18(a) and (b)), and the dense cake layers could not be formed in the tight layers as indicated by Figure 8.18(c). All these SEM images are in good agreement with the results predicted by the network-based fouling model.

8.4.2.3 Foulant Particles with Small Size

In the third system, even smaller polystyrene microspheres (0.053 $\mu m$) were employed to examine the network modeling. The size of the 0.053 $\mu m$ polystyrene microspheres is closer to that of the bonds within the tight layers. Hence, complete internal fouling was expected when the substrate layer was exposed to the feed stream.
The 0.053 $\mu m$ polystyrene microsphere solutions were filtered through both PPVG and VP membranes with both the skin and substrate layers exposed to the feed stream. For the same reasons as mentioned in section 8.4.2.2, the feed concentration was reduced to 0.00025 g/L for 0.053 $\mu m$ polystyrene microspheres.

The plots of the normalized flow versus filtration time and the normalized flow versus particle loading were displayed in Figure 8.19. The solid curves are the network modeling based on the parameters listed in Table 8.1. The model predictions are consistent with the experimental data. It is interesting to note that during the initial filtration the asymmetric membranes with the substrate layer up yielded a lower flux decline while they displayed a higher flux decline over long time filtration. This is in contrast to the observations on the reversed membrane orientation. During the initial filtration, the flux decline was dominated by the pore blockage. When the substrate was exposed to the feed stream, the rate of pore blockage at the skin-substrate interface could be decreased by the porous structure of the substrate layer. As the membrane was highly fouled, a thicker cake layer was formed within the porous structure compared to the cake layer formed on the surface of the skin layer thereby higher hydraulic resistance. The most interesting thing is that the discrepancy between PPVG and VP membranes caused by the 0.14 $\mu m$ polystyrene microspheres could be seen in this case. We can have a better understanding about this issue with the results from network modeling.

Similarly, we calculated the capture rate as a function of filtration time for both the PPVG and VP membranes with the substrate layer up. The calculation
results for the PPVG membrane were plotted in Figure 8.20. The plots are similar to those for the $0.14 \mu m$ polystyrene microspheres as shown by Figure 8.12. More particles were packed due to the higher concentration of particle number for the $0.053 \mu m$ polystyrene microspheres. Figure 8.21 demonstrated the result for the VP membrane. In contrast to the results for $0.14 \mu m$ polystyrene microspheres in Figure 8.13, the regions of particle straining were moved to the lower network layers, and the span in the transverse direction was decreased. We also note that a large number of particles were packed during the long time filtration as indicated by Figure 8.21(c). This indicates that a dense cake layer could have been formed within the blocked regions.

The comparison of SPT and FTP was demonstrated in Figure 8.22 and Figure 8.23 for PPVG and VP membranes, respectively. In Figure 8.22, we can see that less particles were trapped during the filtration in contrast to the results predicted by SPT. This is because most of the bonds were blocked during the initial filtration, and this prevented the particles from flowing into those bonds. Similar results were seen for the VP membranes as shown by Figure 8.23. It is interesting to note that the particle packing primarily occurred within the $z$ bonds as indicated by Figure 8.23(b3). As a result, more particles were trapped within those regions with packed particles (Figure 8.23(b2)).

All this fouling behavior within the asymmetric structures contributed to the reduction of the effective bond size as shown by comparative plots in Figure 8.24. It clearly shows that the $z$ bonds near the bottom surface were significantly decreased
during the filtration for both the PPVG and VP membranes with the substrate layer exposed to the feed stream.

The SEM images for the PPVG membranes fouled by 0.053 \( \mu m \) polystyrene microspheres (0.002 g/L, 2 h) were demonstrated in Figure 8.25. As predicted by the network modeling, almost all particles passed through the substrate layer, and deposited at the skin-substrate interface as shown in Figure 8.25(c). Figure 8.26 shows the SEM images for the VP membranes. In contrast to the image in Figure 8.18(c), packed 0.053 \( \mu m \) polystyrene microspheres were clearly found within the bottom layers as indicated by Figure 8.26(c). This is consistent with the results of the filtration experiments.

8.5 Conclusions

The goal of this work was to extend the network-based fouling model to account for an asymmetric membrane structure. The single bonds in the original network was modified to accommodate the variation of membrane pore density by defining the bond combination, which consists of subbonds. In order to describe the asymmetric profiles of various membrane properties, a mathematical approximation was developed with one adjustable parameter \( N \), which governs the rate of membrane property change along the membrane profile. This mathematical approximation was combined with the fouling model accounting for membrane morphology to theoretically analyze the effects of asymmetric membrane structure on
fouling behavior.

The network modeling was validated by the filtration experiments with two asymmetric membranes having different substructures: PPVG and VP membranes. Polystyrene microspheres with size of 1.01 µm, 0.14 µm, and 0.053 µm were filtered through both PPVG and VP membranes with the skin layer up and the substrate layer up. The interplay between the foulant particle size and asymmetric membrane structures was successfully demonstrated by the network modeling. Both the experimental and modeling results indicated that graded pores could distribute the foulant particles within the membrane structure thereby mitigating the fouling. However, the foulant particle size was much smaller than the pore size of the porous substrate, better performance was obtained by exposing the tight skin layer to the feed stream.

The agreement between the network modeling and the experimental results is good, and it can presumably be improved if more details about the membrane structures were obtained. Despite the large-scale computational effort, the network-based fouling model provides more degrees of freedom for us to design the microfiltration membranes with better fouling resistance.
Table 8.1 Parameters for Constructing Asymmetric Networks

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<th>$\eta_b$</th>
<th>$\varphi_r$</th>
<th>$\varphi_n$</th>
<th>$\epsilon_{ms}$</th>
<th>$N$</th>
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<td></td>
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<td></td>
<td></td>
<td>((\mu m))</td>
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</table>

[1]. $N$ for $\bar{r}_b$ was set to 20.

[2]. $N$ for $\epsilon_{ms}$ was set to 15.
Figure 8.1 Schematic diagram of three-dimensional network for simulating asymmetric membranes
Figure 8.2 Approximation of asymmetric profiles: a) $\eta > 1$; b) $\eta < 1$. 
Figure 8.3 Theoretical analysis of the effects of asymmetric profiles (N) on the normalized flow rate based on the fouling model accounting for asymmetric structures (central blockage with impermeable foulant layer, $\theta=0.64$).
Figure 8.4 The effects of asymmetric hydraulic permeability $K_z$ profiles ($\eta=100$) on the flow streamlines (central blockage with impermeable foulant layer, $\theta=0.64$): a) $N=0.1$; b) $N=1$; c) $N=100$. 
Figure 8.5 The effects of asymmetric hydraulic permeability $K_z$ profiles ($\eta=0.01$) on the flow streamlines: a) $N=0.1$; b) $N=1$; c) $N=100$. 
Figure 8.6 Theoretical analysis of the effects of the depth of impermeable foulant layer with the asymmetric membrane structure ($\eta=0.01$) on the normalized flow rate based on the fouling model accounting for asymmetric structures (central blockage with impermeable foulant layer, $\theta=0.64$).
Figure 8.7 The effects of the depth of impermeable foulant layer within the asymmetric membrane structure ($\eta=0.01$, $N=0.1$) on the flow streamlines: a) $z_f^*=0.1$; b) $z_f^*=0.5$; c) $z_f^*=0.9$. 
Figure 8.8 The effects of the depth of impermeable foulant layer within the asymmetric membrane structure ($\eta=0.01, N=10$) on the flow streamlines: a) $z_f^*=0.1$; b) $z_f^*=0.5$; c) $z_f^*=0.9$. 
Figure 8.9 1.01 µm PS beads (0.005 g/L) filtered through PPVG and VP membranes with skin layer and substrate layer up: a) normalized flow rate versus filtration time; b) normalized flow rate versus particle loading. Solid curves are model calculations based on the parameters in Table 8.1.
Figure 8.10 Scanning electron micrographs of both upper surface and cross-section of PPVG membrane with a) skin layer up and b) substrate layer up fouled by 1.01 µm PS beads (0.00125 g/L, 2 h).
Figure 8.11 0.14 µm PS beads (0.0005 g/L) filtered through PPVG and VP membranes with skin layer and substrate layer up: a) normalized flow rate versus filtration time; b) normalized flow rate versus particle loading. Solid curves are model calculations based on the parameters in Table 8.1.
Figure 8.12 Calculated particle capture rate of each network layer for 0.14 µm PS beads (0.0005 g/L) filtered through PPVG with substrate layer up at 10 psi based on the parameters in Table 8.1: a) the rate of particle straining; b) the rate of particle trapping; c) the rate of particle packing.
Figure 8.13 Calculated particle capture rate of each network layer for 0.14 µm PS beads (0.0005 g/L) filtered through VP with substrate layer up at 12 psi based on the parameters in Table 8.1: a) the rate of particle straining; b) the rate of particle trapping; c) the rate of particle packing.
Figure 8.14 0.14 µm PS beads (0.0005 g/L) filtered through PPVG membrane with substrate layer up at 10 psi: a) SPT ($n_p=20000$); b) FPT ($t=2$ h).
Figure 8.15 0.14 μm PS beads (0.0005 g/L) filtered through VP membrane with substrate layer up at 12 psi: a) SPT ($\eta_p=20000$); b) FPT (t=2 h).
Figure 8.16 The squared ratio of effective bond radius to bond radius versus filtration time for 0.14 µm PS beads (0.0005 g/L) filtered through a) PPVG membrane (10 psi) and b) VP membrane (12 psi) with substrate layer up. Calculations are based on the parameters in Table 8.1.
Figure 8.17 Scanning electron micrographs of the cross-section of PPVG membrane with substrate layer up fouled by 0.14 µm PS beads (0.002 g/L, 10 psi, 2 h). The left panel is the whole cross-section with a white box around the area for high magnification image in the right panel.
Figure 8.18 Scanning electron micrographs of the cross-section of VP membrane with substrate layer up fouled by 0.14 µm PS beads (0.002 g/L, 12 psi, 2 h). The left panel is the whole cross-section with a white box around the area for high magnification image in the right panel.
Figure 8.19 0.053 μm PS beads (0.00025 g/L) filtered through PPVG and VP membranes with skin layer and substrate layer up: a) normalized flow rate versus filtration time; b) normalized flow rate versus particle loading. Solid curves are model calculations based on the parameters in Table 8.1.
Figure 8.20 Calculated particle capture rate of each network layer for 0.053 µm PS beads (0.00025 g/L) filtered through PPVG with substrate layer up at 10 psi based on the parameters in Table 8.1: a) the rate of particle straining; b) the rate of particle trapping; c) the rate of particle packing.
Figure 8.21 Calculated particle capture rate of each network layer for 0.053 µm PS beads (0.00025 g/L) filtered through VP with substrate layer up at 12 psi based on the parameters in Table 8.1: a) the rate of particle straining; b) the rate of particle trapping; c) the rate of particle packing.
Figure 8.22 0.053 μm PS beads (0.00025 g/L) filtered through PPVG membrane with substrate layer up at 10 psi: a) SPT ($n_p=20000$); b) FPT (t=2 h).
Figure 8.23 0.053 μm PS beads (0.00025 g/L) filtered through VP membrane with substrate layer up at 12 psi: a) SPT ($n_p=20000$); b) FPT ($t=2$ h).
Figure 8.24 The squared ratio of effective bond radius to bond radius versus filtration time for 0.053 µm PS beads (0.00025 g/L) filtered through a) PPVG membrane (10 psi) and b) VP membrane (12 psi) with substrate layer up. Calculations are based on the parameters in Table 8.1.
Figure 8.25 Scanning electron micrographs of the cross-section of PPVG membrane with substrate layer up fouled by 0.053 µm PS beads (0.002 g/L, 10 psi, 2 h). The left panel is the whole cross-section with a white box around the area for high magnification image in the right panel.
Figure 8.26 Scanning electron micrographs of the cross-section of VP membrane with substrate layer up fouled by 0.053 μm PS beads (0.002 g/L, 12 psi, 2 h). The left panel is the whole cross-section with a white box around the area for high magnification image in the right panel.
CHAPTER 9 CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

A series of fouling models based on both continuum and statistical approaches were developed for optimizing asymmetric membrane structure. The major conclusions from this work and several implications based on the current studies were summarized below.

9.1.1 A Three-Mechanism Model to Describe Membrane Fouling

A three-mechanism fouling model was developed in CHAPTER 4 by combining pore blockage, cake filtration, and pore constriction. In contrast to the combined fouling model developed by Ho and Zydney [75], this three-mechanism fouling model is able to account for both external fouling and internal fouling. The flux decline within the open area was attributed to the pore constriction by uniform foulant particle adsorption onto the straight-through pore structures. The three model parameters describing the rate of pore blockage ($\alpha$), the rate of pore constriction ($\beta$), and the rate of cake growth ($R'$) all have a clear physical meaning. The relative importance of these fouling mechanisms was investigated by combining the scaling analysis with the plot of $\frac{d^2\tau}{dV^2}$ versus $\frac{dt}{dV}$.

The model calculations were validated by the filtration experiments with four
feed-membrane combinations. Each of these combinations was well designed so that the expected fouling mechanism was dominant during the filtration. All model predictions were shown to be in good agreement with the experimental data. The best fit fouling parameters from the filtration experiments provide deep insight into the complex fouling processes during microfiltration.

9.1.2 Theoretical Analysis of Effects of Asymmetric Structures on External Fouling

In CHAPTER 5, the fouling model accounting for membrane morphology [124] was modified to accommodate asymmetric membrane structures. The permeability ratio indicating pore connectivity and membrane hydraulic resistance was varied in the transverse direction piecewisely to simulate double-layer composite membranes. The model calculations clearly demonstrated how an asymmetric structure affect pressure profiles and flow streamlines. According to the results predicted by our model, the porous membrane structure in the top layer was able to allow the fluid to flow into the blocked region, and the relatively high hydraulic resistance in the bottom layer redistributed the lateral flow for lower net resistance.

The best fit fouling parameters and parameters for membrane morphology were obtained from the filtration experiments with homogeneous membranes. Then, these parameters were applied to the simulations of composite membranes. The model predictions were compared with the experimental data measured from the double-layer membranes having various profiles of both pore connectivity and
hydraulic resistance. The good agreement between theory and experiment indicates that the composite membranes with higher pore connectivity in the upper layer and higher hydraulic resistance in the lower layer have better performance during the filtration in which external fouling is dominant.

### 9.1.3 A-Priori Estimation for Fouling Parameters In the Combined Pore Blockage and Cake Filtration Model

The external fouling parameters in the combined pore blockage and cake filtration model developed by Ho and Zydney [75], i.e., the parameter for pore blockage $\alpha$ and the parameter for cake growth $R'$, were directly correlated to the feed characteristics and the membrane properties based on their physical meanings. The polydispersity of the foulant particles were taken into account so that the mathematical models could have more degrees of freedom to accommodate more complex systems. The partial derivative-based sensitivity analysis was employed to investigate the feed characteristics and membrane properties involved in the mathematical models.

A series of single component solutions, including different sized polystyrene microspheres and proteins, were employed to examine the model predictions. The feed characteristics, including mass fraction of foulant, particle size distribution, cake porosity, and initial resistance of single particle, were measured by independent experiments, and combined with the known membrane properties to estimate the fouling parameters based on the developed mathematical correlations. The model
predictions based on the estimated parameters were in good agreement with the experimental data.

The binary mixture rules were also developed to account for the effects of binary mixtures on the fouling behavior. The complex binary mixtures containing both polystyrene microspheres and proteins were used to examine the model predictions. The flux decline yielded by these binary mixtures was accurately predicted by the model calculations based on the binary mixture rules. It was indicated that the interplay between different foulant particles and filtration membranes had a significant impact on the fouling processes.

9.1.4 A Network-Based Fouling Model Accounting for Asymmetric Membrane Structures

This study described a statistical approach to simulate the fouling processes based on a network representing the realistic membrane structures. The method for constructing a three-dimensional network accounting for various membrane properties was developed. The asymmetric membrane structures were successfully simulated by using a bond combination composed of a cluster of subbonds to substitute for a conventional single bond. The variations of the asymmetric structures were approximated by a power function with an adjustable parameter $N$, which can be used to control the rate of membrane property change. The fouling mechanisms within the network were summarized as particle straining, particle trapping, and particle packing. The corresponding mathematical models were developed based on
the stochastic nature of the particle flow. The permeability of the network can be evaluated by the effective bond size, which is directly related to all fouling mechanisms during the filtration. A single particle test (SPT) based on the network modeling was proposed for a faster theoretical analysis of the fouling processes. The network modeling was compared with the fouling models based on the conventional approaches. It demonstrated that the network modeling is consistent with the conventional fouling models while providing more information about the fouling processes.

The effects of asymmetric membrane structure on the fouling behavior were investigated by the network modeling. The model predictions were validated by the filtration experiments with two asymmetric membranes having different asymmetric profiles. The evolution of the foulant particle distribution within the membrane structures was accurately predicted by the network modeling. Both the experimental results and the results based on the network modeling indicate that the graded porous structures can efficiently prevent the particles with like size from forming a dense cake layer within the membrane structure thereby mitigating the internal fouling. When the size of the foulant particles is much smaller than the average size of the porous substrate, the orientation with tight side facing the feed stream is recommended for better performance.
9.2 Recommendations

The fouling models based on the continuum approaches can help us to understand the fouling processes at a macroscopic scale. However, in order to deliver a explicit solution, many assumptions are required to simplify the realistic processes. As we derived the three-mechanism fouling model, the membranes were referred to as an array of cylindrical pores, and the internal fouling was described by the uniform adsorption of foulant onto the pore walls. Although the fouling parameter for pore constriction \( \beta \) has physical meaning, it is difficult to directly relate \( \beta \) to the feed characteristics and the membrane properties due to the model simplifications. In CHAPTER 7, the permeability reduction caused by the particle trapping was evaluated by the effective bond size. This indicates that the fouling parameter for pore constriction in the continuum model may be interpreted based on the definition of effective bond size to relate to feed characteristics and membrane properties. The adsorption of proteins onto the membrane structure usually involves very small particles (about 10 nm) indicating extremely large-scale computational effort for the modeling at a particle scale. It would be desirable to carry out this study with a powerful computer.

With the modified fouling model accounting for membrane morphology, we optimized the composite membranes composed of two layers under the condition of external fouling. More composite membranes with multilayered structures have been invented. It is worth an effort to extend out current model to account for more complicated structures. However, the effects of the thickness of each layer in the
composite membrane were implicitly ignored in the current study. It is recommended that more efforts would be put into the issue about the layer thickness, which may have significant impact on the fouling behavior as the multilayered structures are applied. In addition, the mathematical method for solving the partial differential equations involved in this model needs to be improved for a faster analysis for the highly asymmetric structures.

The initial resistance of a single particle $R_{c,0}$ is a critical parameter for both the conventional fouling models and the network-based fouling model. As discussed in CHAPTER 6, $R_{c,0}$ is actually a lumped parameter indicating the interaction between the foulant particles and the membrane pores. The measurement of compressibility in CHAPTER 5 also indicated that the operating conditions might have an impact on the value of $R_{c,0}$. Although $R_{c,0}$ could be measured by independent experiments, there is no explicit mathematical model for estimating $R_{c,0}$ based on feed characteristics, membrane properties, and operating conditions. Further studies about $R_{c,0}$ could offer a complete prediction of fouling parameters for various fouling models, and additional insight into the fouling mechanisms involving the interaction between foulant and membrane.

In current studies, most of the structure parameters for constructing the network were somewhat arbitrarily chosen or roughly determined by comparing the predicted hydraulic resistance to the experimental value. It would be desirable to perform a systematic experimental study for investigating the asymmetric membrane structures so that more accurate membrane properties could be provided for network
modeling. For example, the variation of pore size distribution can be determined by taking more SEM images along the entire membrane cross-section.

Both the modified fouling model accounting for membrane morphology and the network-based fouling model were currently focused on the effects of the variation of membrane properties in the transverse direction on the fouling behavior. If the selective skin layer could be distributed into the entire membrane structure with a certain pattern, asymmetric membranes with better performance are more likely to be produced. This study will involve the variation of membrane properties in the horizontal direction. Therefore, more sophisticated models are required to construct the network accounting for the heterogeneous structure. In addition, systematical filtration experiments with asymmetric membranes having more complex substructure are recommended to challenge the network-based fouling model.
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Appendix A: Notation

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<th>Symbol</th>
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<td>$J_0$</td>
<td>Initial filtrate flux</td>
<td>m/s</td>
</tr>
<tr>
<td>$J_b$</td>
<td>Filtrate flux within the blocked area</td>
<td>m/s</td>
</tr>
<tr>
<td>$J_u$</td>
<td>Filtrate flux within the unblocked area</td>
<td>m/s</td>
</tr>
<tr>
<td>$K$</td>
<td>Dimensionless permeability ratio</td>
<td></td>
</tr>
<tr>
<td>$K_z$</td>
<td>Normalized permeability in transverse direction</td>
<td></td>
</tr>
<tr>
<td>$K_i$</td>
<td>Parameter in Eq. (1.55)</td>
<td></td>
</tr>
<tr>
<td>$k$</td>
<td>Darcy permeability</td>
<td>m$^3$/kg</td>
</tr>
<tr>
<td>$k_h$</td>
<td>Darcy permeability in horizontal direction</td>
<td>m$^3$/kg</td>
</tr>
<tr>
<td>$k_{zf}$</td>
<td>Coefficient defined in Eq. (1.17)</td>
<td></td>
</tr>
<tr>
<td>$k_r$</td>
<td>Darcy permeability in radial direction</td>
<td>m$^3$/kg</td>
</tr>
<tr>
<td>$k_z$</td>
<td>Darcy permeability in transverse direction</td>
<td>m$^3$/kg</td>
</tr>
<tr>
<td>$L_b$</td>
<td>Length of network bond</td>
<td>m or $\mu m$</td>
</tr>
<tr>
<td>$L_c$</td>
<td>Thickness of cake layer</td>
<td>m or $\mu m$</td>
</tr>
<tr>
<td>$L_e$</td>
<td>Length of imaginary cake layer channel</td>
<td>m</td>
</tr>
<tr>
<td>$L_m$</td>
<td>Membrane thickness</td>
<td>m</td>
</tr>
<tr>
<td>$M_T$</td>
<td>Moment acting on particle</td>
<td>$N \cdot m$</td>
</tr>
<tr>
<td>$m_p$</td>
<td>Mass of deposited foulant per unit area</td>
<td>kg/m$^2$</td>
</tr>
<tr>
<td>$N$</td>
<td>Parameter for controlling asymmetric membrane profile</td>
<td></td>
</tr>
<tr>
<td>$N_0$</td>
<td>Total number of membrane pores</td>
<td></td>
</tr>
<tr>
<td>$n_e$</td>
<td>Number of network site</td>
<td></td>
</tr>
</tbody>
</table>
Appendix

\( n_s \) Number of network sites covered by one particle

\( n_b \) Number of network bond

\( n_f \) Index defined in Eq. (1.17)

\( n_p \) Number of particles

\( n_s \) Number of membrane pores covered by one particle

\( n_{sb} \) Number of network subbond

\( P \) Probability of a site being open in percolation theory

\( P_c \) Critical probability for percolation threshold

\( P_{wall} \) Probability of particle reaching the tube wall

\( p \) Pressure \( N/m^2 \) or psi

\( p_f \) Pressure of feed stream \( N/m^2 \) or psi

\( p_p \) Pressure of permeate stream \( N/m^2 \) or psi

\( Q \) Flow rate \( m^3/s \)

\( Q_0 \) Flow rate of clean membrane \( m^3/s \)

\( Q_b \) Flow rate within the blocked region \( m^3/s \)

\( Q_s \) Flow rate of a single bond \( m^3/s \)

\( Q_u \) Flow rate within the unblocked region \( m^3/s \)

\( Q_w \) Flow rate of DI water \( m^3/s \)

\( R \) Hydraulic resistance \( m^{-1} \)

\( R' \) Specific resistance of cake layer \( m/kg \)

\( R_c \) Cake layer resistance \( m^{-1} \)

\( R_{c0} \) Initial resistance of single particle \( m^{-1} \)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_e$</td>
<td>Particle retention</td>
<td></td>
</tr>
<tr>
<td>$R_m$</td>
<td>Membrane resistance</td>
<td>$m^{-1}$</td>
</tr>
<tr>
<td>$R_{mf}$</td>
<td>Resistance of internally fouled membrane</td>
<td>$m^{-1}$</td>
</tr>
<tr>
<td>$R_{skin}$</td>
<td>Resistance of skin layer</td>
<td>$m^{-1}$</td>
</tr>
<tr>
<td>$R_{sub}$</td>
<td>Resistance of substrate layer</td>
<td>$m^{-1}$</td>
</tr>
<tr>
<td>$r_p$</td>
<td>Radius of network bond</td>
<td>$m$ or $\mu m$</td>
</tr>
<tr>
<td>$r_{be}$</td>
<td>Effective radius of network bond</td>
<td>$m$ or $\mu m$</td>
</tr>
<tr>
<td>$r_{blocked}$</td>
<td>Radius of blocked region in central blockage</td>
<td>$m$ or $\mu m$</td>
</tr>
<tr>
<td>$r_c$</td>
<td>Radius of cylindrical region</td>
<td>$m$ or $\mu m$</td>
</tr>
<tr>
<td>$r_m$</td>
<td>Radius of clean membrane pore</td>
<td>$m$ or $\mu m$</td>
</tr>
<tr>
<td>$\bar{r}_m$</td>
<td>Mean of membrane pore radius</td>
<td>$m$ or $\mu m$</td>
</tr>
<tr>
<td>$\tilde{r}_m$</td>
<td>Parameter in Eq. (1.39)</td>
<td>$m$ or $\mu m$</td>
</tr>
<tr>
<td>$r_{mf}$</td>
<td>Radius of fouled membrane pore</td>
<td>$m$ or $\mu m$</td>
</tr>
<tr>
<td>$r_{open}$</td>
<td>Radius of unblocked region in central void</td>
<td>$m$ or $\mu m$</td>
</tr>
<tr>
<td>$r_p$</td>
<td>Radius of particle</td>
<td>$m$ or $\mu m$</td>
</tr>
<tr>
<td>$r_{pa}$</td>
<td>Equatorial radius of oblate spheroid</td>
<td>$m$ or $\mu m$</td>
</tr>
<tr>
<td>$r_{pc}$</td>
<td>Polar radius of oblate spheroid</td>
<td>$m$ or $\mu m$</td>
</tr>
<tr>
<td>$r_{pt}$</td>
<td>Particle position in radial direction</td>
<td>$m$ or $\mu m$</td>
</tr>
<tr>
<td>$S$</td>
<td>Solute sieving coefficient</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature</td>
<td>$K$</td>
</tr>
<tr>
<td>$t$</td>
<td>Filtration time</td>
<td>$s$ or $\text{min}$</td>
</tr>
<tr>
<td>$t^*$</td>
<td>Normalized filtration time</td>
<td></td>
</tr>
<tr>
<td>$t_o$</td>
<td>Time of observation for filtration experiment</td>
<td>$s$ or $\text{min}$</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>$t_p$</td>
<td>Time at which the blocked region is first covered by particle</td>
<td>s or min</td>
</tr>
<tr>
<td>$t_p^*$</td>
<td>Normalized time when blocked region is first covered by particle</td>
<td></td>
</tr>
<tr>
<td>$t_\alpha$</td>
<td>Characteristic time for pore blockage</td>
<td>s or min</td>
</tr>
<tr>
<td>$t_\beta$</td>
<td>Characteristic time for pore constriction</td>
<td>s or min</td>
</tr>
<tr>
<td>$t_\gamma$</td>
<td>Characteristic time for cake filtration</td>
<td>s or min</td>
</tr>
<tr>
<td>$V$</td>
<td>Total volume of filtrate</td>
<td>$m^3$ or $mL$</td>
</tr>
<tr>
<td>$V_{feed}$</td>
<td>Volume of feed solution</td>
<td>$m^3$ or $mL$</td>
</tr>
<tr>
<td>$V_m$</td>
<td>Total volume of membrane</td>
<td>$m^3$ or $mL$</td>
</tr>
<tr>
<td>$V_{mp}$</td>
<td>Total volume of membrane pores</td>
<td>$m^3$ or $mL$</td>
</tr>
<tr>
<td>$V_{mpf}$</td>
<td>Total volume of membrane pores after internal fouling</td>
<td>$m^3$ or $mL$</td>
</tr>
<tr>
<td>$V_{PS}$</td>
<td>Volume of aqueous polystyrene microspheres</td>
<td>$m^3$ or $mL$</td>
</tr>
<tr>
<td>$v$</td>
<td>Fluid velocity within network bond</td>
<td>$m/s$</td>
</tr>
<tr>
<td>$v^*$</td>
<td>Critical fluid velocity within network bond</td>
<td>$m/s$</td>
</tr>
<tr>
<td>$v_0$</td>
<td>Fluid velocity within clean network bond</td>
<td>$m/s$</td>
</tr>
<tr>
<td>$v_N$</td>
<td>Normal velocity component of fluid flow</td>
<td>$m/s$</td>
</tr>
<tr>
<td>$v_T$</td>
<td>Tangential velocity component of fluid flow</td>
<td>$m/s$</td>
</tr>
<tr>
<td>$Z$</td>
<td>Coordination number</td>
<td></td>
</tr>
<tr>
<td>$z$</td>
<td>Coordinate perpendicular to the membrane</td>
<td>$m$</td>
</tr>
<tr>
<td>$z_a$</td>
<td>Axial position of network bond</td>
<td>$m$ or $\mu m$</td>
</tr>
<tr>
<td>$z_c$</td>
<td>Thickness of upper layer of composite membrane</td>
<td>$m$</td>
</tr>
<tr>
<td>$z_f$</td>
<td>Depth of foulant layer within the membrane</td>
<td>$m$</td>
</tr>
</tbody>
</table>

**Greek Letters**
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Pore blockage parameter</td>
<td>$m^2/kg$</td>
</tr>
<tr>
<td>$\alpha_V$</td>
<td>Volume of deposited foulant on pore walls per unit foulant mass</td>
<td></td>
</tr>
<tr>
<td>$\beta$</td>
<td>Pore constriction parameter</td>
<td>$kg^{-1}$</td>
</tr>
<tr>
<td>$\varepsilon_c$</td>
<td>Porosity of cake layer</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_m$</td>
<td>Porosity of membrane</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_{ms}$</td>
<td>Porosity of membrane surface</td>
<td></td>
</tr>
<tr>
<td>$\eta$</td>
<td>Membrane property ratio of bottom layer to top layer</td>
<td></td>
</tr>
<tr>
<td>$\eta_b$</td>
<td>Ratio of standard deviation of bond size to average bond size</td>
<td></td>
</tr>
<tr>
<td>$\theta$</td>
<td>Fraction of blocked membrane area</td>
<td></td>
</tr>
<tr>
<td>$\theta_b$</td>
<td>Lumped parameter in Eq. (1.52)</td>
<td></td>
</tr>
<tr>
<td>$\theta_{b0}$</td>
<td>Parameter in Eq. (1.53)</td>
<td></td>
</tr>
<tr>
<td>$\theta_p$</td>
<td>Area fraction based on the total blocked membrane area</td>
<td></td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Boltzmann’s constant</td>
<td>$J/K$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Viscosity of solution</td>
<td>$Pa\cdot s$</td>
</tr>
<tr>
<td>$\xi_m$</td>
<td>Intensity of particle mass from DLS</td>
<td></td>
</tr>
<tr>
<td>$\tilde{\xi}_m$</td>
<td>Relative intensity of particle mass from DLS</td>
<td></td>
</tr>
<tr>
<td>$\bar{\xi}_n$</td>
<td>Intensity of particle number from DLS</td>
<td></td>
</tr>
<tr>
<td>$\tilde{\bar{\xi}}_n$</td>
<td>Relative intensity of particle number from DLS</td>
<td></td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>$kg/m^3$</td>
</tr>
<tr>
<td>$\rho_{PS}$</td>
<td>Density of polystyrene microsphere</td>
<td>$kg/m^3$</td>
</tr>
<tr>
<td>$\rho_p$</td>
<td>Density of foulant particle</td>
<td>$kg/m^3$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Parameter in Eq. (1.39)</td>
<td>$m$ or $\mu m$</td>
</tr>
<tr>
<td>$\sigma_m$</td>
<td>Standard deviation of membrane pore radius</td>
<td>$m$ or $\mu m$</td>
</tr>
</tbody>
</table>
\( \tau \) Tortuosity of cake layer

\( \tau_w \) Local shear stress at the bond wall \( Pa \)

\( \Phi_p \) Diameter of particle \( m \) or \( \mu m \)

\( \Phi_S \) Sphericity

\( \varphi_n \) Bond number ratio of horizontal bond to transverse bond

\( \varphi_r \) Bond size ratio of horizontal bond to transverse bond \( \varphi_n \)

\( \phi_p \) Energy barrier between particle and bond wall \( J \)

\( \omega \) Mass fraction of foulant particle
### Appendix B: Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>BSA</td>
<td>Bovine serum albumin</td>
</tr>
<tr>
<td>CA</td>
<td>Cellulose acetate</td>
</tr>
<tr>
<td>DBF</td>
<td>Deep bed filtration</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>FPT</td>
<td>Filtration particle test</td>
</tr>
<tr>
<td>MBR</td>
<td>Membrane bioreactor</td>
</tr>
<tr>
<td>NFF</td>
<td>Normal flow filtration</td>
</tr>
<tr>
<td>PCTE</td>
<td>Polycarbonate track-etched</td>
</tr>
<tr>
<td>PDE</td>
<td>Partial differential equation</td>
</tr>
<tr>
<td>PES</td>
<td>Polyethersulfone</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SPT</td>
<td>Single particle test</td>
</tr>
<tr>
<td>TFF</td>
<td>Tangential flow filtration</td>
</tr>
</tbody>
</table>
Appendix C: Mathematical Methods and Computer Programs

C.1 Data Collection for Filtration Experiments with Digital Balance

This program was developed with Matlab R2008a (The MathWorks, Ic., MA). It can be used for collecting experimental data from digital balance (PB3002-S, DeltaRange, Mettler Toledo). The serial port number may vary depending on the computer hardware setting.

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%% BalanceFM Version 1.0 %%%%%%%%%%%
clear;
%%%%%Parameters of Measurement
dtp_mea=10; % minimum sampling time s
tf=120*60; % total filtration time min->s
n_mea=tf/dtp_mea; % number of test point

%%%%%Connect to Balance
bal=serial('COM3'); % create serial object
set(bal,'BaudRate',2400); % setbaud rate
set(bal,'Parity','even'); % set parity
set(bal,'DataBits',7); % set data bits
fopen(bal); % open balance
pause; % wait for command to start measurement

V=zeros(n_mea,1); % accumulated filtrate volume
dV=zeros(n_mea,1); % differential filtrate volume
for i=1:n_mea
    fprintf(bal,'SI'); % send command to balance
    tbr1=clock; % the initial time for balance reading
    bda=fscanf(bal); % scan balance to get results
    fbda=sscanf(bda,'%s%s%f%s'); % scan results to generate formated data array
    pbdi=fbda(3,1); % get balance reading from data array mL(g)
    V(i)=pbdi;
    if i==1
        dV(i)=0;
    else
        dV(i)=V(i)-V(i-1);
end

hold on;
subplot(2,1,1);
plot((i-1)*dtp_mea/60,V(i), 'r.');
xlabel('Filtration Time (min)');
ylabel('Total Volume (mL)');
hold on;
subplot(2,1,2);
plot((i-1)*dtp_mea/60,dV(i), 'b.');
xlabel('Filtration Time (min)');
ylabel('dV (mL)');
drawnow;
tbr2=clock; % the ending time for balance reading
pause(dtp_mea-etime(tbr2,tbr1)); % hold for next sample
derase;
end

close(bal); % close balance
delete(bal); % delete balance object

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
C.2 Solving PDE with Variable Coefficients by FV-MG Method

Eq. (5.7) is a partial differential equation with variable coefficients ($K_z$ and $K$). In order to bound the dimensionless radius $r^*$ to be $o(1)$, here, we substitute the radius scale $r_{\text{blocked}}$ with $r_*$ so that $r^* = \frac{r}{r_*}$ ranges from 0 to 1.

Correspondingly, we need to redefine the normalized permeability ratio $K$ which is related to $r_{\text{blocked}}$:

$$K' = \left( \frac{L_m}{r_*} \right)^2 \frac{k_r}{k_z}$$

(10.1)

The relationship between $K$ and $K'$ can be given by Eqs. (10.2) and (10.3) for central blockage model and central void model, respectively:

$$K' = K \theta$$

(10.2)

$$K' = K (1 - \theta)$$

(10.3)

Then, the dimensionless governing equation (5.7) can be rewritten as:

$$\frac{1}{r^*} \frac{\partial}{\partial r^*} \left( r^{*} K' \frac{\partial p^*}{\partial r^*} \right) + \frac{\partial}{\partial z^*} \left( K' \frac{\partial p^*}{\partial z^*} \right) = 0$$

(10.4)

Finite volume method (box integration method) is a popular approach by starting from the integral conservative forms of boundary value problems and using numerical integrations to construct conservative difference schemes on irregular grids [292]. In terms of the finite volume method, the discretization of the dimensionless governing equation (10.4) can be obtained by numerically integrating each term in Eq. (10.4) over a mesh cell (shade area in Figure C 1, points A, B, D, and E are the
midpoints of neighboring nodes) to give:

\[
\int K_z K' \frac{\partial}{\partial r^*} \left( r^{**} \frac{\partial p^*}{\partial r} \right) dr^* dz^* = K_z (z_j^*) K'(z_j^*) \left( \frac{p_D - p_C}{r_{i+1}^{**} - r_i^{**}} + \frac{r_{i+1}^{**} + r_i^{**}}{2} \right) \frac{z_{j+1}^* - z_{j-1}^*}{2}
\]

\[
(10.5)
\]

\[
\int r^{**} \frac{\partial}{\partial z^*} \left( K_z \frac{\partial p^*}{\partial z} \right) dz^* dr^* = r_i^{**} \left( \frac{p_E - p_C}{z_{j+1}^* - z_j^*} K_z (z_{j+1/2}^*) \right) \frac{z_{j+1}^* - z_{j-1}^*}{2}
\]

\[
(10.6)
\]

The same scheme was applied to each boundary condition to obtain a complete linear algebraic equations for \( p_A, \ p_B, \ p_C, \ p_D, \) and \( p_E \) at each node on a given mesh:

\[
A_p P^* = f_p
\]

\[
(10.7)
\]

\( A_p \) and \( f_p \) are the matrix and source vector based on Eqs. (10.5) and (10.6), respectively. \( P^* \) is the unknown vector for \( p^* \) at each mesh node. This discretization is a five-point stencil scheme with accuracy to \( (r_{i+1}^{**} - r_i^{**})^2 \) and \( (z_{j+1}^* - z_j^*)^2 \).

In order to concentrate the mesh points in the region of steepest change \( (r^{**} = 0, r_B^{**}, \text{or} \ 1, \ z^* = 0, z_C^*, \text{or} \ 1) \), an adaptable mesh transformation was used:

\[
\begin{cases}
  x_i = \frac{1}{2} \left[ 2 (i - 1) \frac{\zeta}{n_e} \right]^{1+\zeta} & \text{at } 0 \leq x_i \leq \frac{1}{2} \\
  1 - \frac{1}{2} \left[ 2 - 2 (i - 1) \frac{\zeta}{n_e} \right]^{1+\zeta} & \text{at } \frac{1}{2} < x_i \leq 1
\end{cases}
\]

\[
(10.8)
\]

where \( \zeta \) is the normalized length of the region whose endpoints have the concentrated mesh points. For example, for the blocked region in radial direction,
is equal to \( r^*_b \); for the upper layer of the composite membrane, \( \zeta \) is equal to \( z^*_z \). 

\( n_e \) is the number of the elements within the given region, and \( i_e \) denotes the \( i^{th} \) element. When Eq. (10.8) is applied to the radial direction, \( x_i \) is defined as \( \frac{r^{**}}{\zeta} \), whereas \( \frac{z^*}{\zeta} \) is for the transverse direction. The mesh transformation based on Eq. (10.8) is plotted in Figure C 2. It shows that the larger the special region is, the more mesh points are concentrated around the endpoints of this region.

There are a number of iterative methods to solve the linear equations, e.g., Jacobi and Gauss-Seidel schemes. However, most of these conventional methods are characterized by global poor convergence rates when matrix \( A_p \) is highly ill-conditioned. In the study of CHAPTER 5, the highly asymmetric membrane structures will yield a high condition number for matrix \( A_p \). Therefore, we employ the multigrid method (MG) to solve the linear equations (10.7). The multigrid strategy [293] combines two complementary schemes: i) the high-frequency components of the error are reduced applying iterative methods; ii) the low-frequency error components are reduced by a coarse-grid correction procedure.

There are two basic linear operators in the MG method, i.e., prolongation operator \( I_{2h}^h \) and restriction operator \( I_{2h}^{2h} \). The operator \( I_{2h}^h \) linearly maps the coarse grid \( \Omega^{2h} \) to the fine grid \( \Omega^h \). On the other hand, \( I_{2h}^{2h} \) linearly maps the fine grid to the coarse grid. If the matrix on the fine grid is \( A_p \), the matrix \( A_p' \) on the coarse grid can be obtained by:
The basic MG procedure includes four steps:

i. Relax $A_p^r P^r = f_p$ on $\Omega^h$ with successive overrelaxation (SOR) to get $\tilde{P}^r$.

The overrelaxation factor $\omega_{\text{SOR}}$ was set to 0.8 to keep the smoothing properties of SOR [294].

ii. Restrict the error to the coarse grid $\Omega^{2h}$ by:

$$f_p^{2h} = L_{I}^{2h} f_p - A_p \tilde{P}^r$$

iii. Smooth the low-frequency error on the coarse grid by exactly solving:

$$A_p^{2h} e^{2h} = f_p^{2h}$$

iv. Correct the solution on fine grid by interpolating $e^{2h}$ to the fine grid:

$$P^* = \tilde{P}^r + e^h$$

$$e^h = I_{2h}^h e^{2h}$$

A four-level multigrid scheme was employed in our studies for solving Eq. (10.7) as schematically shown in Figure C 3. The complete FV-MG method was coded with Matlab R2008a (The MathWorks, Ic., MA):

```matlab
clear;

%%%%% Model Parameters
%% imported parameters
CBV=1; % 0==central blockage 1==central void
```

...
theta=0.25; % fraction of blocked area
dzup=0.98; % the normalized thickness of upper layer
Kc=1e30; % Kc=(kz at z=0)*Rp*u/dm
K=@(z) 0.*(z<=dzup)+0.*(z>dzup); % K(z)=(dm/rc)^2*kr/kz
KKz=@(z) 1.*(z<=dzup)+1.*(z>dzup); % Kz(z)=kz/(kz at z=0)

%%%%% calculated parameters
rb=theta^0.5*(CBV==0)+(1-theta)^0.5*(CBV==1); % radius of blocked area
% control the boundary condition on membrane surface
if CBV==0
    KKc=@(r) Kc.*(r<=rb)+1e-30.*(r>rb);
else
    KKc=@(r) 1e-30*(r<rb)+Kc*(r>=rb);
end
KK=@(z) K(z).*(1-theta).^0; % adjust K for high fraction of blocked area

%%%%% Grid Generator
%%%%% grid parameters
GC=1; % 0==regular grid 1==adjusted grid
% set sections in r direction
dr1=rb;
dr2=1-rb;
% set sections in z direction
dz1=dzup;
dz2=1-dzup;
ner0=15; % minimum element number in z direction
zez0=15; % minimum element number in z direction
ner01=3+ceil((ner0-6)*dr1); % minimum r element number in section 1
ner02=ner0-ner01; % minimum r element number in section 2
nez01=3+ceil((nez0-6)*dz1); % minimum z element number in section 1
nez02=nez0-nez01; % minimum element number in section 2 in z direction
m=4; % total levels of grid
ner1=ner01*2^(m-1); % number of elements in section 1 in r direction
ner2=ner02*2^(m-1); % number of elements in section 2 in r direction
ner=ner1+ner2; % number of elements in r direction
nez1=nez01*2^(m-1); % number of elements in section 1 in z direction
nez2=nez02*2^(m-1); % number of elements in section 2 in z direction
nez=nez1+nez2; % number of elements in z direction

%%%%% generate the regular grid
rr=zeros(ner+1,1);
zz=zeros(nez+1,1);
for i=2:ner
    rr(i)=rr(i-1)+(dr1/ner1)*(i<=(ner1+1))+(dr2/ner2)*(i>(ner1+1));
end
rr(ner+1)=1;

for i=2:nez
    zz(i)=zz(i-1)+(dz1/nez1)*(i<=(nez1+1))+(dz2/nez2)*(i>(nez1+1));
end
zz(nez+1)=1;

%%%%% generate the adjusted grid
adg=@(x,w)
0.5.*((x./0.5).*(x<=0.5)).*(1+w).*(x<=0.5)+((0.5+0.5.*((1-(x-0.5)./0.5).*(1+w))).*(x>0.5));
% concentrate points to the edge 0<=x<=1
r=zeros(ner+1,1);
z=zeros(nez+1,1);
if GC==0
    r=rr;
z=zz;
else
    for i=1:ner+1
        if rr(i)<=dr1
            r(i)=dr1*adg(rr(i)/dr1,dr1);
        else
            r(i)=dr1+dr2*adg((rr(i)-dr1)/dr2,dr2);
        end
    end
    for i=1:nez+1
        if zz(i)<=dz1
            z(i)=dz1*adg(zz(i)/dz1,dz1);
        else
            z(i)=dz1+dz2*adg((zz(i)-dz1)/dz2,dz2);
        end
    end
end

%%%%% generate the grid coordinate
CG=0; % 0==Do Not Generate Grid Coordinate 1==Generate Grid Coordinate
if CG==1
    rk=zeros((ner+1)*(nez+1),1);
    zk=zeros((ner+1)*(nez+1),1);
    k=0;
for \( j=1:nez+1 \)
    for \( i=1:ner+1 \)
        \( k=k+1 \);
        \( rk(k)=r(i) \);
        \( zk(k)=z(j) \);
    end
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%% Matrix Generator
%%%%% node parameters
nr=zeros(m,1); \% number of nodes in r direction
nz=zeros(m,1); \% number of nodes in z direction
for \( i=1:m \)
    nr(i)=ner0*2^(i-1)+1;
    nz(i)=nez0*2^(i-1)+1;
end
%%%%% generate grids for each levels
rm=zeros(nr(m),m); \% coordinate in r direction for each level of grid
zm=zeros(nz(m),m); \% coordinate in z direction for each level of grid
for \( j=1:m \)
    for \( i=1:nr(j) \)
        rm(i,j)=r((i-1)*2^(m-j)+1);
    end
    for \( i=1:nz(j) \)
        zm(i,j)=z((i-1)*2^(m-j)+1);
    end
end
%%%%% pretreatment
rd=zeros(nr(m)-1,m); \% rd(i)=r(i)+r(i+1)
dr=zeros(nr(m)-1,m); \% dr(i)=r(i+1)-r(i)
dz=zeros(nz(m)-1,m); \% dz(i)=z(i+1)-z(i)
Kci=zeros(nr(m),m); \% Kci(i)=KKc(rm(i))
Kj=zeros(nz(m)-1,m); \% Kj(i)=KK(z(i))
Kzj=zeros(nz(m)-1,m); \% Kzj(i)=KKz(z(i))
Kzh=zeros(nz(m)-1,m); \% Kzh(i)=KKz(z2h(i)/2)
for \( j=1:m \)
    for \( i=1:nr(j) \)
        rd(i,j)=rm(i,j)+rm(i+1,j);
        dr(i,j)=rm(i+1,j)-rm(i,j);
        Kci(i,j)=KKc(rm(i,j));
    end
    Kci(nr(j),j)=KKc(rm(nr(j),j));
end
for i=1:nz(j)-1
    dz(i,j)=zm(i+1,j)-zm(i,j);
    Kj(i,j)=KK(zm(i,j));
    Kzj(i,j)=KKz(zm(i,j));
    Kzh(i,j)=KKz((zm(i,j)+zm(i+1,j))/2);
end
end
%%%%% calculate the matrix dimension for each levels
nv=zeros(m,1);
for i=1:m
    nv(i)=nr(i)*(nz(i)-1);
end
%%%%% calculate the value of coefficients on strips
Av=zeros(nv(m),m); % value of coefficient of p(j-1,i)
Bv=zeros(nv(m),m); % value of coefficient of p(j,i-1)
Cv=zeros(nv(m),m); % value of coefficient of p(j,i)
Dv=zeros(nv(m),m); % value of coefficient of p(j,i+1)
Ev=zeros(nv(m),m); % value of coefficient of p(j+1,i)
bv=zeros(nv(m),m); % value of source term
for h=1:m
    k=0;
    for i=1:nr(h)
        k=k+1;
        if i==1
            Cv(k,h)=-1*(2*Kzj(1,h)*Kj(1,h)/dr(i,h)^2+2*Kzh(1,h)/zm(2,h)^2+2*Kzj(1,h)/(Kci(i,h)*zm(2,h)));
        end
        Dv(k,h)=2*Kzj(1,h)*Kj(1,h)/dr(i,h)^2;
        Ev(k,h)=2*Kzh(1,h)/zm(2,h)^2;
        bv(k,h)=-1*(2*Kzj(1,h)/(Kci(i,h)*zm(2,h)));
    end
else
    Cv(k,h)=-1*(Kzj(1,h)*Kj(1,h)*(rd(i,h)/dr(i,h)+rd(i-1,h)/dr(i-1,h))/(rm(i,h)*dr(i-1,h)+(rd(i,h)+dr(i-1,h)))/(Kci(i,h)*zm(2,h))); % C4
    Dv(k,h)=Kzj(1,h)*Kj(1,h)*rd(i,h)/(rm(i,h)*dr(i-1,h)+(rd(i,h)+dr(i-1,h)))*dr(i-1,h)); % D4
    Ev(k,h)=2*Kzh(1,h)/zm(2,h)^2; % E4
    bv(k,h)=-1*(2*Kzj(1,h)/(Kci(i,h)*zm(2,h)))); % -1*b4
end
elseif i==nr(h)

else
    Cv(k,h)=2*Kzj(1,h)*Kj(1,h)/dr(i-1,h)^2; % B6
    Cv(k,h)=-1*(2*Kzj(1,h)*Kj(1,h)*rd(i-1,h)/dr(i-1,h)^2+2*Kzh(1,h)/zm(2,h)^2+2*Kzj(1,h)/(Kci(i,h)*zm(2,h)))); % C6
    Ev(k,h)=2*Kzh(1,h)/zm(2,h)^2; % E6
bv(k,h)=-1*(2*Kzj(1,h)/(Kci(i,h)*zm(2,h))); % -1*b6
end
end
for j=2:nz(h)-1
for i=1:nr(h)
k=k+1;
    if i==1
        Av(k,h)=2*Kzh(j-1,h)/((dz(j,h)+dz(j-1,h))*dz(j-1,h)); % A2
        Cv(k,h)=-1*(2*(Kzj(j,h)*Kj(j,h)/dr(i,h)^2)+2*(Kzh(j,h)/dz(j,h)+Kzh(j-1,h)/dz(j-1,h))/dz(j,h)+dz(j-1,h)))); % C2
        Dv(k,h)=2*Kzj(j,h)*Kj(j,h)/dr(i,h)^2; % D2
        Ev(k,h)=(2*Kzh(j,h)/((dz(j,h)+dz(j-1,h))*dz(j,h)))*(j==nz(h)-1); % E2
    elseif i>1&&i<nr(h)
        Av(k,h)=2*Kzh(j-1,h)/((dz(j,h)+dz(j-1,h))*dz(j-1,h)); % A1
        Bv(k,h)=Kzj(j,h)*Kj(j,h)*rd(i-1,h)/(rm(i,h)*(dr(i,h)+dr(i-1,h)))*dr(i-1,h)); % B1
        Cv(k,h)=-1*(Kzj(j,h)*Kj(j,h)*(rd(i,h)/dr(i,h)+rd(i-1,h)/dr(i-1,h))/(rm(i,h)*(dr(i,h)+dr(i-1,h)))+2*(Kzh(j,h)/dz(j,h)+Kzh(j-1,h)/dz(j-1,h))/dz(j,h)+dz(j-1,h)))); % C1
        Dv(k,h)=Kzj(j,h)*Kj(j,h)*rd(i,h)/(rm(i,h)*(dr(i,h)+dr(i-1,h)))*dr(i-1,h)); % D1
        Ev(k,h)=(2*Kzh(j,h)/((dz(j,h)+dz(j-1,h))*dz(j,h)))*(j==nz(h)-1); % E1
    elseif i==nr(h)
        Av(k,h)=2*Kzh(j-1,h)/((dz(j,h)+dz(j-1,h))*dz(j-1,h)); % A3
        Bv(k,h)=2*Kzj(j,h)*Kj(j,h)/dr(i-1,h)^2; % B3
        Cv(k,h)=-1*(2*(Kzj(j,h)*Kj(j,h)/dr(i-1,h)^2)+2*(Kzh(j,h)/dz(j,h)+Kzh(j-1,h)/dz(j-1,h))/dz(j,h)+dz(j-1,h)))); % C3
        Dv(k,h)=(2*Kzh(j,h)/((dz(j,h)+dz(j-1,h))*dz(j,h)))*(j==nz(h)-1); % E3
    end
end
end
end

%%%%% calculate the location of coefficients on strips
Ac=zeros(nv(m),m); % location of coefficient of p(j-1,i)
Bc=zeros(nv(m),m); % location of coefficient of p(j,i-1)
Dc=zeros(nv(m),m); % location of coefficient of p(j,i+1)
Ec=zeros(nv(m),m); % location of coefficient of p(j+1,i)
for h=1:m
    for i=1:nv(h)
        Ac(i,h)=((i-nr(h))<=0)*nv(h)+i-nr(h);
    end
end
\begin{align*}
Bc(i,h) &= ((i-1) \leq 0) \cdot n_v(h) + i - 1; \\
Dc(i,h) &= i + 1 - ((i + 1) > n_v(h)) \cdot n_v(h); \\
Ec(i,h) &= i + n_r(h) - ((i + n_r(h)) > n_v(h)) \cdot n_v(h); \\
\end{align*}

\item[	extbf{end}] 
\item[	extbf{end}] 
\text{ni} = \text{zeros}(m-1,1); \ % \text{the \ number \ of \ element \ in \ matrix \ I} \ n_v(i) \cdot n_v(i-1) 
\text{for} \ i = 1:m-1 
\quad \text{ni}(i) &= (3 \cdot (n_z(i+1)-1)/2-1) \cdot (n_r(i+1)+(n_r(i+1)-1)/2); 
\text{end} 
\text{II} = \text{zeros}([ni(m-1),3,m-1]); \ % \text{matrix \ I} \ 1=value \ 2=row \ 3=column 
\text{for} \ h = 1:m-1 
\quad k = 0; 
\text{for} \ i = 1:n_r(h) 
\quad \text{ii} = 2 \cdot (i-1)+1; 
\quad \text{jj} = 2 \cdot (j-1)+1; 
\quad k = k + 1; 
\quad \text{II}(k,1,h) &= 1; 
\quad \text{II}(k,2,h) &= (jj-1) \cdot n_r(h+1)+ii; 
\quad \text{II}(k,3,h) &= (j-1) \cdot n_r(h)+i; 
\quad k = k + 1; 
\quad \text{II}(k,1,h) &= dz(jj+1,h+1)/(dz(jj,h+1)+dz(jj+1,h+1)); 
\quad \text{II}(k,2,h) &= jj \cdot n_r(h+1)+ii; 
\quad \text{II}(k,3,h) &= (j-1) \cdot n_r(h)+i; 
\quad \text{if} \ j < n_z(h)-1 
\quad k = k + 1; 
\quad \text{II}(k,1,h) &= dz(jj,h+1)/(dz(jj,h+1)+dz(jj+1,h+1)); 
\quad \text{II}(k,2,h) &= jj \cdot n_r(h+1)+ii; 
\quad \text{II}(k,3,h) &= j \cdot n_r(h)+i; 
\quad \text{end} 
\quad \text{if} \ i < n_r(h) 
\quad \text{if} \ rm(i+1,h) == rb 
\quad k = k + 1; 
\quad \text{II}(k,1,h) &= (dr(ii,h+1)+dr(ii-1,h+1)+dr(ii-2,h+1))/(dr(ii-1,h+1)+dr(ii-2,h+1)); 
\quad \text{II}(k,2,h) &= (jj-1) \cdot n_r(h+1)+ii+1; 
\quad \text{II}(k,3,h) &= (j-1) \cdot n_r(h)+i; 
\quad k = k + 1; 
\quad \text{II}(k,1,h) &= -1 \cdot dr(ii,h+1)/(dr(ii-1,h+1)+dr(ii-2,h+1)); 
\quad \text{II}(k,2,h) &= (jj-1) \cdot n_r(h+1)+ii+1; 
\quad \text{II}(k,3,h) &= (j-1) \cdot n_r(h)+i-1; 
\quad k = k + 1; 
\quad \text{II}(k,1,h) &= dz(jj+1,h+1)/(dz(jj,h+1)+dz(jj+1,h+1)) \cdot ((dr(ii,h+1)+dr(ii-1,h+1)+dr(ii-2,h+1))/(dr(ii-1,h+1)+dr(ii-2,h+1)));
II(k, 2, h) = jj * nr(h+1) + ii + 1;
II(k, 3, h) = (j-1) * nr(h) + i;
k = k + 1;
II(k, 1, h) = -1*(dz(jj+1, h+1)/(dz(jj, h+1) + dz(jj+1, h+1)))*(dr(ii, h+1)/(dr(ii-1, h+1) + dr(ii-2, h+1)));
II(k, 2, h) = jj * nr(h+1) + ii + 1;
II(k, 3, h) = (j-1) * nr(h) + i - 1;

if j < nz(h) - 1
    k = k + 1;
    II(k, 1, h) = (dz(jj, h+1)/(dz(jj, h+1) + dz(jj+1, h+1)))*(dr(ii, h+1)/(dr(ii-1, h+1) + dr(ii-2, h+1)));
    II(k, 2, h) = jj * nr(h+1) + ii + 1;
    II(k, 3, h) = j * nr(h) + i;
k = k + 1;
    II(k, 1, h) = -1*(dz(jj, h+1)/(dz(jj, h+1) + dz(jj+1, h+1)))*(dr(ii, h+1)/(dr(ii-1, h+1) + dr(ii-2, h+1)));
    II(k, 2, h) = jj * nr(h+1) + ii + 1;
    II(k, 3, h) = (j-1) * nr(h) + i - 1;
end

elseif rm(i, h) == rb
    k = k + 1;
    II(k, 1, h) = (dr(ii+1, h+1) + dr(ii+2, h+1) + dr(ii+3, h+1))/(dr(ii+2, h+1) + dr(ii+3, h+1));
    II(k, 2, h) = (jj-1) * nr(h+1) + ii + 1;
    II(k, 3, h) = (j-1) * nr(h) + i + 1;
k = k + 1;
    II(k, 1, h) = -1*dr(ii+1, h+1)/(dr(ii+2, h+1) + dr(ii+3, h+1));
    II(k, 2, h) = (jj-1) * nr(h+1) + ii + 1;
    II(k, 3, h) = (j-1) * nr(h) + i + 2;
k = k + 1;
    II(k, 1, h) = (dz(jj+1, h+1)/(dz(jj, h+1) + dz(jj+1, h+1)))*(dr(ii+1, h+1) + dr(ii+2, h+1) + dr(ii+3, h+1))/(dr(ii+2, h+1) + dr(ii+3, h+1));
    II(k, 2, h) = jj * nr(h+1) + ii + 1;
    II(k, 3, h) = (j-1) * nr(h) + i + 1;
k = k + 1;
    II(k, 1, h) = -1*(dz(jj+1, h+1)/(dz(jj, h+1) + dz(jj+1, h+1)))*(dr(ii+1, h+1)/(dr(ii+2, h+1) + dr(ii+3, h+1)));
    II(k, 2, h) = jj * nr(h+1) + ii + 1;
    II(k, 3, h) = (j-1) * nr(h) + i + 2;
if j < nz(h) - 1
    k = k + 1;
    II(k, 1, h) = (dz(jj, h+1)/(dz(jj, h+1) + dz(jj+1, h+1)))*(dr(ii+1, h+1) + dr(ii+2, h+1) + dr(ii+3, h+1))/(dr(ii+2, h+1) + dr(ii+3, h+1));
    II(k, 2, h) = (jj-1) * nr(h+1) + ii + 1;
    II(k, 3, h) = (j-1) * nr(h) + i + 2;
end


\begin{verbatim}

, h+1));
II(1, 2, h) = jj * nr(h+1) + ii + 1;
II(1, 3, h) = j * nr(h) + i + 1;
k = k + 1;
II(1, 1, h) = -1 * \left(\frac{dz(jj, h+1)}{dz(jj, h+1) + dz(jj+1, h+1)}\right) \left(\frac{dr(ii+1, h+1)}{dr(ii+2, h+1) + dr(ii+3, h+1)}\right);
II(1, 2, h) = jj * nr(h+1) + ii + 1;
II(1, 3, h) = j * nr(h) + i + 2;

end

else

k = k + 1;
II(1, 1, h) = \frac{dr(ii+1, h+1)}{dr(ii, h+1) + dr(ii+1, h+1)};
II(1, 2, h) = (jj-1) * nr(h+1) + ii + 1;
II(1, 3, h) = (j-1) * nr(h) + i;
k = k + 1;
II(1, 1, h) = \frac{dz(jj+1, h+1)}{dz(jj, h+1) + dz(jj+1, h+1)} \left(\frac{dr(ii+1, h+1)}{dr(ii, h+1) + dr(ii+1, h+1)}\right);
II(1, 2, h) = jj * nr(h+1) + ii + 1;
II(1, 3, h) = (j-1) * nr(h) + i;
k = k + 1;
II(1, 1, h) = \frac{dz(jj+1, h+1)}{dz(jj, h+1) + dz(jj+1, h+1)} \left(\frac{dr(ii, h+1)}{dr(ii, h+1) + dr(ii+1, h+1)}\right);
II(1, 2, h) = jj * nr(h+1) + ii + 1;
II(1, 3, h) = (j-1) * nr(h) + i + 1;

if j < nz(h) - 1

k = k + 1;
II(1, 1, h) = \left(\frac{dz(jj, h+1)}{dz(jj, h+1) + dz(jj+1, h+1)}\right) \left(\frac{dr(ii+1, h+1)}{dr(ii, h+1) + dr(ii+1, h+1)}\right);
II(1, 2, h) = jj * nr(h+1) + ii + 1;
II(1, 3, h) = j * nr(h) + i;
k = k + 1;
II(1, 1, h) = \left(\frac{dz(jj, h+1)}{dz(jj, h+1) + dz(jj+1, h+1)}\right) \left(\frac{dr(ii, h+1)}{dr(ii, h+1) + dr(ii+1, h+1)}\right);
II(1, 2, h) = jj * nr(h+1) + ii + 1;
II(1, 3, h) = j * nr(h) + i + 1;

end

end

end
end

end
\end{verbatim}

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end

h=3;
IH3=sparse(II(1:ni(h),2,h),II(1:ni(h),3,h),II(1:ni(h),1,h)); % linear operator from h=3 to h=4
h=2;
IH2=sparse(II(1:ni(h),2,h),II(1:ni(h),3,h),II(1:ni(h),1,h)); % linear operator from h=2 to h=3
h=1;
IH1=sparse(II(1:ni(h),2,h),II(1:ni(h),3,h),II(1:ni(h),1,h)); % linear operator from h=1 to h=2
MF=zeros(nv(m)*5,3,m);
for h=1:m
    for i=1:nv(h)
        MF((i-1)*5+1,1,h)=Av(i,h);
        MF((i-1)*5+1,2,h)=i;
        MF((i-1)*5+1,3,h)=Ac(i,h);
        MF((i-1)*5+2,1,h)=Bv(i,h);
        MF((i-1)*5+2,2,h)=i;
        MF((i-1)*5+2,3,h)=Bc(i,h);
        MF((i-1)*5+3,1,h)=Cv(i,h);
        MF((i-1)*5+3,2,h)=i;
        MF((i-1)*5+3,3,h)=i;
        MF((i-1)*5+4,1,h)=Dv(i,h);
        MF((i-1)*5+4,2,h)=i;
        MF((i-1)*5+4,3,h)=Dc(i,h);
        MF((i-1)*5+5,1,h)=Ev(i,h);
        MF((i-1)*5+5,2,h)=i;
        MF((i-1)*5+5,3,h)=Ec(i,h);
    end
end
RKz=@(z) 1./KKz(z);
inRKz=quadl(RKz,0,1,1e-7);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%% Equation Solver with SOR+FMG
x=zeros(nv(m),m); % solutions for each level
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% FMG at level 2
h=2;
M2=sparse(MF(1:nv(h)*5,2,h),MF(1:nv(h)*5,3,h),MF(1:nv(h)*5,1,h)); % operator matrix at level 2
F2=bv(1:nv(h),h); % source term at level 2
x(1:nv(h),h)=M2\F2; % exact solution at level 2
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

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h=4;
x(1:nv(h),h)=IH3*(IH2*x(1:nv(h-2),h-2));  \% interpolation to level 4
F4=bv(1:nv(h),h);  \% source term at level 4
M4=sparse(MF(1:nv(h)*5,2,h),MF(1:nv(h)*5,3,h),MF(1:nv(h)*5,1,h));  \% operator
matrix at fine grid
[mrr4,mcc4,mvv4]=find(M4');  \% find nonzero elements in M4
k=1;
mnz4=zeros(nv(4),1);  \% number of nonzero elements in each row of M4
for i=1:length(mvv4)
  if k==mcc4(i)
    mnz4(k)=mnz4(k)+1;
  else
    k=k+1;
    mnz4(k)=1;
  end
end
M3=IH3'*M4*IH3;  \% calculate operator at level 3
[mrr3,mcc3,mvv3]=find(M3');  \% find nonzero elements in M3
k=1;
mnz3=zeros(nv(3),1);  \% number of nonzero elements in each row of M3
for i=1:length(mvv3)
  if k==mcc3(i)
    mnz3(k)=mnz3(k)+1;
  else
    k=k+1;
    mnz3(k)=1;
  end
end
M2=IH2'*M3*IH2;  \% calculate operator at level 2
[mrr2,mcc2,mvv2]=find(M2');  \% find nonzero elements in M2
k=1;
mnz2=zeros(nv(2),1);  \% number of nonzero elements in each row of M2
for i=1:length(mvv2)
  if k==mcc2(i)
    mnz2(k)=mnz2(k)+1;
  else
    k=k+1;
    mnz2(k)=1;
  end
end
e=1;
i=1;
while i<1000& &e>1e-7
  h=4;
x0 = x(1:nv(h),h); % record initial x at fine grid
wr4 = 0.8; % relaxation factor of level 4
for ik = 1:2 % relaxation at fine grid
    k = 1;
    for ii = 1:nv(h)
        xs = 0;
        for im = 1:mnz4(ii)
            if mrr4(k) ~= mcc4(k)
                xs = xs + mvv4(k)*x(mrr4(k),h);
            else
                mvi = mvv4(k);
            end
            k = k + 1;
        end
        x(ii,h) = (1-wr4)*x(ii,h) + wr4*(F4(ii) - xs)/mvi;
    end
end
h = 3;
F3 = IH3'*((F4 - M4*x(1:nv(h+1),h+1))); % restriction to level 3
x(:,h) = 0; % set initial value of x at level 3
wr3 = 0.8; % relaxation factor of level 3
for ik = 1:2 % relaxation at level 3
    k = 1;
    for ii = 1:nv(h)
        xs = 0;
        for im = 1:mnz3(ii)
            if mrr3(k) ~= mcc3(k)
                xs = xs + mvv3(k)*x(mrr3(k),h);
            else
                mvi = mvv3(k);
            end
            k = k + 1;
        end
        x(ii,h) = (1-wr3)*x(ii,h) + wr3*(F3(ii) - xs)/mvi;
    end
end
h = 2;
F2 = IH2'*((F3 - M3*x(1:nv(h+1),h+1))); % restriction to level 2
x(1:nv(h),h) = M2\F2; % exact solution at level 2
h = 3;
x(1:nv(h),h) = x(1:nv(h),h) + IH2*x(1:nv(h-l),h-l); % interpolation to level 3
wr3 = 0.8; % relaxation factor of level 3
for ik = 1:2 % relaxation at level 3
    k = 1;
end
for ii=1:nv(h)
    xs=0;
    for im=1:mnz3(ii)
        if mrr3(k)~=mcc3(k)
            xs=xs+mvv3(k)*x(mrr3(k),h);
        else
            mvi=mvv3(k);
        end
        k=k+1;
    end
    x(ii,h)=(1-wr3)*x(ii,h)+wr3*(F3(ii)-xs)/mvi;
end
end

h=4;
F4=x(1:nv(h),h)+IH3*x(1:nv(h-1),h-1);
wr4=0.8;
for ik=1:2
    k=1;
    for ii=1:nv(h)
        xs=0;
        for im=1:mnz4(ii)
            if mrr4(k)~=mcc4(k)
                xs=xs+mvv4(k)*x(mrr4(k),h);
            else
                mvi=mvv4(k);
            end
            k=k+1;
        end
        x(ii,h)=(1-wr4)*x(ii,h)+wr4*(F4(ii)-xs)/mvi;
    end
    e=norm(x(1:nv(h),h)-x0)/norm(x(1:nv(h),h));
end
inrdpdz=0;
for i=1:nr(m)-1
    inrdpdz=inrdpdz+(r(i+1)*dpdzs(i+1)+r(i)*dpdzs(i))*dr(i,m)/2;
    if i==ner1
        inrdpdz1=inrdpdz;
    end
end
inrdpdz2=inrdpdz-inrdpdz1;

%%%%% calculate J
RKz=@(z) 1./KKz(z);
inRKz=quadl(RKz,0,1,1e-7);
NJt=-2*inRKz*inrdpdz; % total NJ
NJ1=-2*inRKz*inrdpdz1; % NJ within r<rb
NJ2=(NJt-NJ1*rb^2)/(1-rb^2); % NJ within r>rb

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
C.3 Network-Based Fouling Model

The program for the network-based fouling model consists four elements. The first program (NWFM_MS) includes functions for constructing the network based on the studied membrane structures. The second program (NWFM_iPD) calculates the initial pressure distribution within the network, and estimates the hydraulic resistance. The third program (NWFM_PF) estimates the particle capacity for the network based on the feed characteristics. The fourth program (NWFM_PF_FT) injects the particles to the network and determine their final status for permeability evaluation.

NWFM_MS

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% Membrane Parameters
Lm=125*1e-6; % membrane thickness um->m

ZP=0; % pore style in z direction 0=random 1=straight through
rma_s=0.0225*1e-6; % average pore size at membrane surface um->m
eta_s=0.01; % the ratio of variance to rma at membrane surface
kappar_s=0.5; % pore size ratio rma_h/rma_z at membrane surface
kappap_s=0.8; % pore density ratio pd_h/pd_z at membrane surface
em_s=0.35; % porosity at membrane surface
epez_s=1; % fraction of permeable z pores at membrane surface
epeh_s=1; % fraction of permeable h pores at membrane surface

rma_b=0.4*1e-6; % average pore size at membrane bottom um->m
eta_b=0.5; % the ratio of variance to rma at membrane bottom
kappar_b=0.9; % pore size ratio rma_h/rma_z at membrane bottom
kappap_b=1; % pore density ratio pd_h/pd_z at membrane bottom
em_b=0.6; % porosity at membrane bottom
epez_b=1; % fraction of permeable z pores at membrane bottom
\[ epeh_b = 1; \] \% fraction of permeable \( h \) pores at membrane bottom

\[ \text{Nu}_rma = 0.5; \] \% profile parameter for average pore size
\[ \text{Nu}_eta = 0.5; \] \% profile parameter for pore size variance
\[ \text{Nu}_kappar = 0.5; \] \% profile parameter for pore size ratio
\[ \text{Nu}_kappap = 0.5; \] \% profile parameter for pore density ratio
\[ \text{Nu}_em = 15; \] \% profile parameter for porosity
\[ \text{Nu}_epez = 0.5; \] \% profile parameter for \( epez \)
\[ \text{Nu}_epeh = 0.5; \] \% profile parameter for \( epeh \)

\text{Net Work Parameters}

\[ \text{nex} = 50; \] \% number of element in \( x \) direction
\[ \text{ney} = 50; \] \% number of element in \( y \) direction
\[ \text{nez} = 100; \] \% number of element in \( z \) direction

\[ dLm = Lm / \text{nez}; \] \% bond length in \( z \) direction
\[ dLxy = 0.9153e-6; \] \% bond length in \( x \) or \( y \) direction

\text{Profile functions}

\[ \text{fra} = @(\text{nezi}) \% \text{fra}
\begin{align*}
(rma_s * ((1-rma_b/rma_s) * ((\text{nezi} - \text{nez}) / (\text{nez} - 1)).^\text{Nu}_rma + rma_b/rma_s));
\end{align*}
\%
\text{profile of rma}
\]
\[ \text{feta} = @(\text{nezi}) \% \text{feta}
\begin{align*}
(eta_s * ((1-eta_b/eta_s) * ((\text{nezi} - \text{nez}) / (\text{nez} - 1)).^\text{Nu}_eta + eta_b/eta_s));
\end{align*}
\%
\text{profile of pore size variance}
\]
\[ \text{fkappar} = @(\text{nezi}) \% \text{fkappar}
\begin{align*}
(kappar_s * ((1-kappar_b/kappar_s) * ((\text{nezi} - \text{nez}) / (\text{nez} - 1)).^\text{Nu}_kappar + kappar_b/kappar_s));
\end{align*}
\%
\text{profile of pore size ratio \( rma_x/rma_z = rma_y/rma_z \)}
\]
\[ \text{fkappap} = @(\text{nezi}) \% \text{fkappap}
\begin{align*}
(kappap_s * ((1-kappap_b/kappap_s) * ((\text{nezi} - \text{nez}) / (\text{nez} - 1)).^\text{Nu}_kappap + kappap_b/kappap_s));
\end{align*}
\%
\text{profile of pore density ratio \( pd_x/pd_z = pd_y/pd_z \)}
\]
\[ \text{fem} = @(\text{nezi}) \% \text{fem}
\begin{align*}
(em_s * ((1-em_b/em_s) * ((\text{nezi} - \text{nez}) / (\text{nez} - 1)).^\text{Nu}_em + em_b/em_s));
\end{align*}
\%
\text{profile of porosity}
\]
\[ \text{fepez} = @(\text{nezi}) \% \text{fepez}
\begin{align*}
(epez_s * ((1-epez_b/epez_s) * ((\text{nezi} - \text{nez}) / (\text{nez} - 1)).^\text{Nu}_epez + epez_b/epez_s));
\end{align*}
\%
\text{profile of epez}
\]
\[ \text{fepeh} = @(\text{nezi}) \% \text{fepeh}
\begin{align*}
(epeh_s * ((1-epeh_b/epeh_s) * ((\text{nezi} - \text{nez}) / (\text{nez} - 1)).^\text{Nu}_epeh + epeh_b/epeh_s));
\end{align*}
\%
\text{profile of epeh}
\]
\[ \text{npx} = \text{zeros}(\text{nez},1); \] \% number of pores in \( x \) direction at each layer
\[ \text{npy} = \text{zeros}(\text{nez},1); \] \% number of pores in \( y \) direction at each layer
\[ \text{npz} = \text{zeros}(\text{nez},1); \] \% number of pores in \( z \) direction at each layer
\[ \text{dnsbx} = \text{zeros}(\text{nez},1); \] \% number of \( x \) subbonds per bond combination at each
layer
dnsby=zeros(nez,1); % number of y subbonds per bond combination at each layer
dnsbz=zeros(nez,1); % number of z subbonds per bond combination at each layer
nsbx=zeros(nez,1); % number of subbonds in x direction at each layer
nsby=zeros(nez,1); % number of subbonds in y direction at each layer
nsbz=zeros(nez,1); % number of subbonds in z direction at each layer
nsbex=zeros(nez,1); % number of effective bonds in x direction at each layer
nsbey=zeros(nez,1); % number of effective bonds in y direction at each layer
nsbez=zeros(nez,1); % number of effective bonds in z direction at each layer
eta=feta(1:1:nez)'; % pore size variance ratio at each layer
kappar=fkappar(1:1:nez)'; % pore size ratio at each layer
kappap=fkappap(1:1:nez)'; % pore density ratio at each layer
em=fem(1:1:nez)'; % porosity at each layer
rmza=fra(1:1:nez)'; % average bond radius in z direction m
epez=fepez(1:1:nez)'; % epez at each layer
epeh=fepeh(1:1:nez)'; % epeh at each layer
rmxa=rmza.*kappar; % average bond radius in x direction m
rmya=rmza.*kappar; % average bond radius in y direction m
emc=zeros(nez,1); % realistic porosity
for k=1:nez
    npz(k)=round(dLxy^2*nex*ney*em(k)/(pi*rmza(k)^2));
    npx(k)=round(npz(k)*kappap(k)*dLm*dLxy*ney*nex/(dLxy^2*nex*ney));
    npx(k)=npx(k);
    dnsbex(k)=(round(npx(k)/(nex*ney)))*(npx(k)>(nex*ney))+(npx(k)<=(nex*ney));
    if dnsbex(k)<(npx(k)/(nex*ney))
        rounddn=(npx(k)/(nex*ney)-dnsbex(k))/dnsbex(k);
        if rounddn>0.2
            dnsbex(k)=dnsbex(k)+1;
        end
    end
    nsbex(k)=dnsbex(k)*nex*ney;
    nsbex(k)=(nsbex(k)<=npx(k))+npx(k)*((nsbex(k)>npx(k)));
    dnsby(k)=(round(npy(k)/(nex*ney)))*(npy(k)>(nex*ney))+(npy(k)<=(nex*ney));
    if dnsby(k)<(npy(k)/(nex*ney))
        rounddn=(npy(k)/(nex*ney)-dnsby(k))/dnsby(k);
        if rounddn>0.2
            dnsby(k)=dnsby(k)+1;
        end
end
dnsby(k)=dnsby(k)+1;
end
end
nsby(k)=nsby(k)*nex*ney;
nsbey(k)=nsby(k)*(nsby(k)<=npy(k))+npy(k)*(nsby(k)>npy(k));
dnsbz(k)=(round(npz(k)/(nex*ney)))*(npz(k)>=(nex*ney))+npz(k)<=(nex*ney));
if dnsbz(k)<(npz(k)/(nex*ney))
   rounddn=(npz(k)/(nex*ney)-dnsbz(k))/dnsbz(k);
   if rounddn>0.2
      dnsbz(k)=dnsbz(k)+1;
   end
end
nsbz(k)=dnsbz(k)*nex*ney;
sbez(k)=nsbz(k)*(nsbz(k)<=npz(k))+npz(k)*(nsbz(k)>npz(k));
end
rmx=zeros(ney,nex,nez); % radius of x subbonds
rmy=zeros(ney,nex,nez); % radius of y subbonds
rmz=zeros(ney,nex,nez); % radius of z subbonds
for k=1:nez
   rmx(:,:,k)=PoreSizeD(nex, ney, rmxa(k), rmxa(k)*eta(k));
   rmy(:,:,k)=PoreSizeD(nex, ney, rmya(k), rmya(k)*eta(k));
   rmz(:,:,k)=PoreSizeD(nex, ney, rmza(k), rmza(k)*eta(k));
end
nrmx=ones(ney,nex,nez); % number of x subbonds
nrmy=ones(ney,nex,nez); % number of y subbonds
nrmz=ones(ney,nex,nez); % number of z subbonds
nrmt=zeros(nez,1); % total number of x subbonds
nrmyt=zeros(nez,1); % total number of y subbonds
nrmzt=zeros(nez,1); % total number of z subbonds
nebxt=zeros(nez,1); % total effective x bonds
nebym=zeros(nez,1); % total effective y bonds
nebzt=zeros(nez,1); % total effective z bonds
for k=1:nez
   nrmx(:,:,k)=ones(ney,nex)*dnsbx(k);
   nvoid=nsbx(k)-round(nsbex(k)*epeh(k)); % number of void subbonds
   if nvoid>0
      xpv=round(random('unif',1,nex*ney,nvoid,1));
      [nrmx(:,:,k) rmx(:,:,k) nsbex(k)]=PoreSizeV(nex, ney, nvoid, xpv, nrmx(:,:,k), rmx(:,:,k));
   end
   nrmy(:,:,k)=ones(ney,nex)*dnsby(k);
nvoid = nsby(k) - round(nsbey(k)*epeh(k));
if nvoid > 0
    xpv = round(random('unif', 1, nex*ney, nvoid, 1));
    [nrmy(:, :, k) rmy(:, :, k) nsbey(k)] = PoreSizeV(nex, ney, nvoid, xpv,
        nrmy(:, :, k), rmy(:, :, k));
end
nrmz(:, :, k) = ones(ney, nex)*dnsbz(k);
nvoid = nsbz(k) - round(nsbz(k)*epez(k));
if nvoid > 0
    if ZP == 0
        xpv = round(random('unif', 1, nex*ney, nvoid, 1));
    else
        if k == 1
            xpv = round(random('unif', 1, nex*ney, nvoid, 1));
        else
            if ((nsbz(k) == nsbz(k-1)) + (nsbez(k) == nsbez(k-1))) > 0
                xpv = round(random('unif', 1, nex*ney, nvoid, 1));
            end
        end
    end
end
[nrmz(:, :, k) rmz(:, :, k) nsbez(k)] = PoreSizeV(nex, ney, nvoid, xpv,
        nrmz(:, :, k), rmz(:, :, k));
end
end
for k = 1:nez
    for j = 1:ney
        for i = 1:nex
            nrmxt(k, 1) = nrmxt(k, 1) + nrmx(j, i, k);
            nrmyt(k, 1) = nrmyt(k, 1) + nrmy(j, i, k);
            nrmzt(k, 1) = nrmzt(k, 1) + nrmz(j, i, k);
            nebxt(k, 1) = nebxt(k, 1) + (nrmx(j, i, k) > 0);
            nebyt(k, 1) = nebyt(k, 1) + (nrmy(j, i, k) > 0);
            nebzt(k, 1) = nebzt(k, 1) + (nrmz(j, i, k) > 0);
        end
    end
end

NWFM_iPD

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% Membrane Parameters
RVM = 0;  % 0==the same orintation l==reversed orintation
Appendix

% Operation Parameters

dp=2*6896.551724; % trans-membrane pressure psi->Pa
u=1e-3; % viscosity Pas

if RVM==1

    eta=flipud(eta);
    kappar=flipud(kappar);
    kappap=flipud(kappap);
    em=flipud(em);
    rmx=flipud(rmx);
    nsbx=flipud(nsbx);
    nsbex=flipud(nsbex);
    dnsbx=flipud(dnsbx);
    fnrmx=nrmx;
    nrmxt=flipud(nrmxt);
    for k=1:nez
        rmx(:,:,k)=flipud(frmx(:,:,nez-k+1));
        nrmx(:,:,k)=flipud(fnrmx(:,:,nez-k+1));
    end
    nrmxt=flipud(nrmxt);
    nebxt=flipud(nebxt);
    rmya=flipud(rmya);
    nsby=flipud(nsby);
    nsbey=flipud(nsbey);
    dnsby=flipud(dnsby);
    frmy=rmy;
    fnrmy=nrmy;
    for k=1:nez
        rmy(:,:,k)=flipud(frmy(:,:,nez-k+1));
        nrmy(:,:,k)=flipud(fnrmy(:,:,nez-k+1));
    end
    nrmyt=flipud(nrmyt);
    nebyt=flipud(nebyt);
    rmza=flipud(rmza);
    nsbz=flipud(nsbz);
    nsbez=flipud(nsbz);
    dnsbz=flipud(dnsbz);
    frmz=rmz;
    fnrmz=nrmz;
    for k=1:nez
        rmz(:,:,k)=flipud(frmz(:,:,nez-k+1));
        nrmz(:,:,k)=flipud(fnrmz(:,:,nez-k+1));
    end
end
nrmzt=flipud(nrmzt);
nebzt=flipud(nebzt);

Rs=ones(ney,nex)*1e-30;  \% resistance at membrane surface m-1
ARst=zeros(ney,nex);  \% total A/(u*Rs) at membrane surface for each bond
for j=1:ney
    for i=1:nex
        ARst(j,i)=(nrmz(j,i,1)+(nrmz(j,i,1)==0))*pi.*rmz(j,i,1).^2./(u.*Rs(j,i));
    end
end

Akxt=zeros(ney,nex,nez);  \% total initial A*k/dL for each x bond
Akyt=zeros(ney,nex,nez);  \% total initial A*k/dL for each y bond
Akzt=zeros(ney,nex,nez);  \% total initial A*k/dL for each z bond
for k=1:nez
    for j=1:ney
        for i=1:nex
            ib=(k-1)*nex*ney+(j-1)*nex+i;
            Akxt(j,i,k)=(nrmx(j,i,k)+(nrmx(j,i,k)==0))*pi.*rmx(j,i,k).^4./
            (8*u*dLxy);  \% total initial A*k/dL for each x bond
            Akyt(j,i,k)=(nrmy(j,i,k)+(nrmy(j,i,k)==0))*pi.*rmy(j,i,k).^4./
            (8*u*dLxy);  \% total initial A*k/dL for each y bond
            Akzt(j,i,k)=(nrmz(j,i,k)+(nrmz(j,i,k)==0))*pi.*rmz(j,i,k).^4./
            (8*u*dLm);  \% total initial A*k/dL for each z bond
        end
    end
end

Np0=zeros(nez*nex*ney,1);  \% initial value of normalized pressure at each node
Np=(p-pb)/(ps-pb)
for k=1:nez
    if k>1
        Akzta=0;
        for ki=1:nez
            Akzta=Akzta+(dnsbz(k-1)*pi*rmza(k-1)^4/8*u*dLm)/((dnsbz(ki)*pi*
            *rmza(ki)^4/8*u*dLm));
        end
    end
    for j=1:ney
        for i=1:nex
            ib=(k-1)*nex*ney+(j-1)*nex+i;
if $k=1$
    \[ Np0(ib)=1; \]
else
    \[ ib2=(k-2)*nex*ney+(j-1)*nex+i; \]
    \[ Np0(ib)=abs(Np0(ib2)-1/Akzta); \]
end
end
end

Av=zeros(ney,nex,nez);
Bv=zeros(ney,nex,nez);
Cv=zeros(ney,nex,nez);
Dv=zeros(ney,nex,nez);
Ev=zeros(ney,nex,nez);
Fv=zeros(ney,nex,nez);
fv=zeros(ney,nex,nez);

[Av Bv Cv Dv Ev Fv fv]=MaxNp(nex,ney,nez,ARst,Akxt,Akyt,Akzt,Av,Bv,Cv,Dv,Ev,Fv,Gv,fv);

Ac=zeros(ney,nex,nez);
Bc=zeros(ney,nex,nez);
Cc=zeros(ney,nex,nez);
Dc=zeros(ney,nex,nez);
Ec=zeros(ney,nex,nez);
Fc=zeros(ney,nex,nez);
Gc=zeros(ney,nex,nez);

for $k=1:nez$
    for $j=1:ney$
        for $i=1:nex$
            npc=(k-1)*nex*ney+(j-1)*nex+i;
            Ac(j,i,k)=npc-nex*ney+(k==1)*nez*nex*ney;
            Bc(j,i,k)=npc-nex+(j==1)*nex*ney;
            Cc(j,i,k)=npc-1+(i==1)*nex;
            Dc(j,i,k)=npc;
            Ec(j,i,k)=npc+1-(i==nex)*nex;
            Fc(j,i,k)=npc+nex-(j==ney)*nex*ney;
            Gc(j,i,k)=npc+nex*ney-(k==nez)*nez*nex*ney;
        end
    end
end
e0=1e-5;
Np=Np0;
for $ie=1:10$
    [Np e Qtsp

Appendix

Npk]=NodeNp_VPGRC(nex,ney,nez,e0,Np,Akzt,Av,Ac,Bv,Bc,Cv,Cc,Dv,Dc,Ev,Ec,Fv,Fc,Gv,Gc,fv);
    if  e<=e0
        break;
    end
end

Qts=Qtsp*dp;  % total surface flow rate m3/s
Js=Qts/(dLxy^2*nex*ney);  % average surface flux m/s
Rm=dp/(Js*u);  % total membrane resistance m-1;

NWFM_PF

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% Operation Parameters
dp=2.5*6896.551724;  % trans-membrane pressure psi->Pa

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% Particle Parameters
rp=0.125*1e-6;  % particle size um->m
Cb=0.0025;  % particle concentration g/L->kg/m3
rhop=1050;  % particle density kg/m3
ep=0.34;  % porosity of particle layer
Rp0=5.58e9;  %

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% Capture Probability Parameters
epm=0.34;  % porosity of particle layer within bonds
H=2.2981e-21;  % Hamaker constant PVDF=2.2981e-21 PES=2.6477e-21
z0=5e-9;  % distance between particle and bond wall m
hrm=0.001;  % relative roughness h/rm
Hz2=H/z0^2;

% effective radius of subonds m
rmxe=rmx;  % effective radius of x subonds m
rmye=rmy;  % effective radius of y subonds m
rmze=rnz;  % effective radius of z subonds m
Rse=Rs;
ARste=ARst;
Akxt=Akx;
Akyt=Aky;
Akz=Akz;
npA=((1-ep)/(4*pi*rp^3/3))^(2/3);  % particle number per membrane area
SUex=zeros(ney,nex,2);  % surface status 1=surface particle 0/n 2=cake particle 0/n
SUex_max = dLxy^2 * npA; % maximum capacity of surface element
if SUex_max > 0.66
    SUex_max = round(SUex_max);
else
    SUex_max = -1 * round(1/SUex_max);
end

% external status of subbonds 1 = entry 1 2 = entry 2
SBex_x = zeros(ney, nex, nez, 2);
SBex_y = zeros(ney, nex, nez, 2);
SBex_z = zeros(ney, nex, nez, 2);

% maximum capacity of external status
SBex_x_max = round(dLxy * dLm * npA);
if SBex_x_max == 0
    SBex_x_max = 1;
end
SBex_y_max = round(dLxy * dLm * npA);
if SBex_y_max == 0
    SBex_y_max = 1;
end
SBex_z_max = round(dLxy^2 * npA);
if SBex_z_max == 0
    SBex_z_max = 1;
end

% internal status of subbonds 1 = fully packed 0/1 2 = capacity per subbond 3 = accumulative number of particles
SBin_x = zeros(ney, nex, nez, 3);
SBin_y = zeros(ney, nex, nez, 3);
SBin_z = zeros(ney, nex, nez, 3);
for k = 1:nez
    for j = 1:ney
        for i = 1:nex
            SBin_x(j, i, k, 2) = round((1 - epm) .* rmx(j, i, k).^2 .* dLxy ./ (4 * rp^3 / 3) .* (rmx(j, i, k) >= rp);
            SBin_y(j, i, k, 2) = round((1 - epm) .* rmy(j, i, k).^2 .* dLxy ./ (4 * rp^3 / 3) .* (rmy(j, i, k) >= rp);
            SBin_z(j, i, k, 2) = round((1 - epm) .* rmz(j, i, k).^2 .* dLm ./ (4 * rp^3 / 3)) .* (rmz(j, i, k) >= rp);
        end
    end
end

NWFM_PF_FT
Appendix

nf=240; % number of filtration step
dtf=zeros(nf,1); % length of time step s
dtmin=ones(nf,1)*30; % initial minimum length of time step s
Qf=zeros(nf,2); % filtration flow rate m3/s 1=flow rate 2=error
np=zeros(nf,1); % number of particles per time step
% average effective pore size m
rmxaf=zeros(nez,nf);
rmya=zeros(nez,nf);
rmaf=zeros(nez,nf);
% variance of effective pore size m
sigma_rx=zeros(nez,nf);
sigma_ry=zeros(nez,nf);
sigma_rz=zeros(nez,nf);
% total flow rate at each layer m3/s
Qxtf=zeros(nez,nf);
Qytf=zeros(nez,nf);
Qztf=zeros(nez,nf);
CUf=zeros(ney,nex,nf); % surface particle distribution
% trapped particle distribution
CTxf=zeros(nez,nf);
CTyf=zeros(nez,nf);
CTzf=zeros(nez,nf);
% packed particle distribution
CPxf=zeros(nez,nf);
CPyf=zeros(nez,nf);
CPzf=zeros(nez,nf);
% stained particle distribution
CSxf=zeros(nez,nf);
CSyf=zeros(nez,nf);
CSzf=zeros(nez,nf);
CHf=zeros(ney,nex,nf); % pass particle distribution
% rm^2/rme^2
rm2rme2x=ones(ney,nex,nez);
rm2rme2y=ones(ney,nex,nez);
rm2rme2z=ones(ney,nex,nez);
e0=1e-4;
for ie=1:10
    [Np e Qtsp
        Npk]=NodeNp_VPGRC(nex,ney,nez,e0,Np,Akzt,Av,Ac,Bv,Bc,Cv,Cc,Dv,
            Dc,Ev,Ec,Fv,Fc,Gv,Gc,fv);
    if e<=e0
        break;
\begin{verbatim}
end
end
Qf0=Qtsp*dp; % initial flow rate m^3/s
% initial average effective pore size m
rmxaf0=zeros(nez,1);
rmym0=zeros(nez,1);
rmzaf0=zeros(nez,1);
% initial variance of effective pore size m
sigma_rx0=zeros(nez,1);
sigma_ry0=zeros(nez,1);
sigma_rz0=zeros(nez,1);
% initial total flow rate at each layer m^3/s
Qxtf0=zeros(nez,1);
Qytf0=zeros(nez,1);
Qztf0=zeros(nez,1);
for k=1:nez
    [~,sigma_rx0(k)] = PoreSizeA(nex, ney, nrmx(:,:,k),
    nrmxt(k), rmx(:,:,k));
    [~,sigma_ry0(k)] = PoreSizeA(nex, ney, nrmy(:,:,k),
    nrmyt(k), rmy(:,:,k));
    [~,sigma_rz0(k)] = PoreSizeA(nex, ney, nrmz(:,:,k),
    nrmzt(k), rmz(:,:,k));
    Qxtf0(k,1)=FlowRateA(nex, ney, Akxt(:,:,k), Npk(:,:,k:(k+1)), dp,
    1);
    Qytf0(k,1)=FlowRateA(nex, ney, Akyt(:,:,k), Npk(:,:,k:(k+1)), dp,
    2);
    Qztf0(k,1)=FlowRateA(nex, ney, Akzt(:,:,k), Npk(:,:,k:(k+1)), dp,
    3);
end
for inf=1:nf
    while dtf(inf)<dtmin(inf)
        PF=zeros(1,6); % particle status C1=jn  C2=in  C3=kn  C4=bond
        indix = C5=1(surface)/2(trapped)/3(packed)/4(stained)/5(pass)
        C6=total time s
        [PF(1) PF(2)]=NWEntry(nex, ney, Akzte,Np);
        PF(4)=6;
        PF(5)=EntryStrain(PF(1),PF(2),rp,rmz,SUex);
        if PF(5)==0
            PF(3)=PF(3)+1;
        end
        while PF(5)==0
            [bix IP dNp
             BJ]=NodeDR(PF(1),PF(2),nex,ney,nez,rmx,rmy,rmz,SBex_
x,SBex_y,SBex_z,SBin_x,SBin_y,SBin_z,Akxt,Akxy,Akzt,Np,dLm, dLxy);
if IP==1
  [PF(1) PF(2) PF(3)]=PreviousNode(PF(1),PF(2),PF(3),PF(4),nex,ney);
  if PF(3)>0
    PF(5)=3;
  else
    PF(5)=1;
  end
else
  PF(4)=bix;
end
if PF(5)==0
  [PF(4) PF(5)] =SubBondStrain(PF(1),PF(2),PF(3),rp,rmx,rmy,rmz,nex,ney,BJ,bix);
end
if PF(5)==0
  [PF(5) Jp dLs]=SubBondTrap(bix,PF(1),PF(2),PF(3),rp,dNp,dp,dLm,dLxy,rmx,rmy,rmz,rmye,rmze,SBin_x,SBin_y,SBin_z,H2z,hrm,u,nex,ney);
end
if PF(5)==0
  [PF(4) PF(2) PF(3)]=NextNode(PF(1),PF(2),PF(3),PF(4),nex,ney);
  PF(6)=PF(6)+dLs/Jp;
  if PF(3)>nez
    PF(5)=5;
  end
end
if PF(5)==1
  [SUex jin]=Change_IU(PF(1),PF(2),nex,ney,SUex_max,SUex);
  [Rse ARste]=ChangeK_IU(jin,Rp0,rp,ep,u,rmz(:,1),nrmz(:,1),dLxy,SUex,Rse,ARste);
  if SUex_max>0
    nmax=SUex_max;
    CUf(PF(1),PF(2),inf)=CUf(PF(1),PF(2),inf)+nmax;
  else
    nmax=1;
    nc=length(jin(:,1));
end
for inc=1:nc
    CUf(jin(inc,1),jin(inc,2),inf)=CUf(jin(inc,1),jin(inc,2),inf)+nmax;
end
end
elseif PF(5)==2
    [SBin_x SBin_y SBin_z]
    nmax]=Change_IT(PF(1),PF(2),PF(3),PF(4),nex,ney,nrmx,nrmy, nrmz,SBin_x,SBin_y,SBin_z);
    [rmxe rmye rmze rm2rme2x rm2rme2y rm2rme2z Akxte Akyte Akzte]=ChangeK_IT(PF(1),PF(2),PF(3),PF(4),nex,ney,rp,Rp0,u,dLm,dLxy,rmx,rmx,rmx,nrmx,nrmy,nrmz,rmye,rmze,rm2rme 2x,rm2rme2y,rm2rme2z,Akxte,Akyte,Akzte);
    [CTxf(:,inf) CTyf(:,inf) CTzf(:,inf)]=Cont_CPF(PF(3),PF(4),CTxf(:,inf),CTyf(:,inf), CTzf(:,inf),nmax);
elseif PF(5)==3
    [SBin_x SBin_y SBin_z]
    nmax]=Change_IP(PF(1),PF(2),PF(3),PF(4),nex,ney,nrmx,nrmy, nrmz,SBin_x,SBin_y,SBin_z);
    [rmxe rmye rmze rm2rme2x rm2rme2y rm2rme2z Akxte Akyte Akzte]=ChangeK_IP(PF(1),PF(2),PF(3),PF(4),nex,ney,rp,u,epm, dLm,dLxy,rmx,rmx,rmx,nrmx,nrmy,nrmz,rmx,rmze,rm2rme 2x,rm2rme2y,rm2rme2z,Akxte,Akyte,Akzte);
    [CPxf(:,inf) CPyf(:,inf) CPzf(:,inf)]=Cont_CPF(PF(3),PF(4),CPxf(:,inf),CPyf(:,inf), CPzf(:,inf),nmax);
elseif PF(5)==4
    [SBex_x SBex_y SBex_z]
    nmax]=Change_IS(PF(1),PF(2),PF(3),PF(4),nex,ney,SBex_x_max,SBex_y_max,SBex_z_max,SBex_x,SBex_y,SBex_z);
    [rmxe rmye rmze rm2rme2x rm2rme2y rm2rme2z Akxte Akyte Akzte]=ChangeK_IS(PF(1),PF(2),PF(3),PF(4),nex,ney,Rp0,u,dLm,dLxy,rmx,rmx,rmx,nrmx,nrmy,nrmz,rmx,rmze,rm2rme 2x,rm2rme2y,rm2rme2z,Akxte,Akyte,Akzte);
    [CSxf(:,inf) CSyf(:,inf) CSzf(:,inf)]=Cont_CPF(PF(3),PF(4),CSxf(:,inf),CSyf(:,inf),CSzf(:,inf),CS zf(:,inf),nmax);
elseif PF(5)==5
    nmax=1;
    CHf(PF(1),PF(2),inf)=CHf(PF(1),PF(2),inf)+nmax;
end
if inf==1
\[
dtf(\text{inf}) = dtf(\text{inf}) + nmax \times 4 \pi r_p^3 \rho_p/(C_B \cdot Q_f 0 \times 3);
\]
\[
\text{else}
\]
\[
dtf(\text{inf}) = dtf(\text{inf}) + nmax \times 4 \pi r_p^3 \rho_p/(C_B \cdot Q_f(\text{inf}-1) \times 3);
\]
\[
\text{end}
\]
\[
\text{if}
\]
\[
dtmin(\text{inf}) < PF(6)
\]
\[
dtmin(\text{inf}) = PF(6);
\]
\[
\text{end}
\]
\[
np(\text{inf}) = np(\text{inf}) + nmax;
\]
\[
\text{end}
\]

\[
\text{[Av Bv Cv Dv Ev Fv Gv fv]} = \text{MaxNp}(\text{nex, ney, nez, ARste, Akxte, Akyte, Akzte, Av, Bv, Cv, Dv, Ev, Fv, Gv, fv});
\]
\[
e_0 = 1e-4;
\]
\[
\text{for} \ i_e = 1:100
\]
\[
\text{[Np e Qtsp Npk]} = \text{NodeNp_VPGRC}(\text{nex, ney, nez, e0, Np, Akzte, Av, Ac, Bv, Bc, Cv, Cc, Dv, Dc, Ev, Ec, Fv, Fc, Gv, Gc, fv});
\]
\[
\text{if} \ e \leq e_0
\]
\[
\text{break};
\]
\[
\text{end}
\]
\[
\text{end}
\]
\[
Q_f(\text{inf},1) = Qtsp \times dp;
\]
\[
Q_f(\text{inf},2) = e;
\]
\[
\text{for} \ k = 1:nez
\]
\[
\text{[rmxaf(k, inf) sigma_rx(k, inf)] = PoreSizeA(nex, ney, nrmx(:, :, k), nrmx(k), rmx(:, :, k))};
\]
\[
\text{[rmyaf(k, inf) sigma_ry(k, inf)] = PoreSizeA(nex, ney, nrmy(:, :, k), nrmy(k), rmy(:, :, k))};
\]
\[
\text{[rmzaf(k, inf) sigma_rz(k, inf)] = PoreSizeA(nex, ney, nrmz(:, :, k), nrmz(k), rmz(:, :, k))};
\]
\[
\text{Qxtf(k, inf) = FlowRateA(nex, ney, Akxte(:, :, k), Npk(:, :, k:(k+1)), dp, 1)};
\]
\[
\text{Qytf(k, inf) = FlowRateA(nex, ney, Akyte(:, :, k), Npk(:, :, k:(k+1)), dp, 2)};
\]
\[
\text{Qztf(k, inf) = FlowRateA(nex, ney, Akzte(:, :, k), Npk(:, :, k:(k+1)), dp, 3)};
\]
\[
\text{end}
\]
\[
NQ = Q_f(\text{inf}, 1)/Q_f0;
\]
\[
\text{end}
\]
Figure C 1 Schematic diagram of finite volume method for solving PDE with variable coefficients in a cylindrical coordinate system.
Figure C.2 Adaptable mesh transformation
Figure C 3 Adaptable grids for multigrid method: a) grid at level 1 (coarse grid) b) grid at level 2 c) grid at level 3 d) grid at level 4 (finest grid).