Fundamentals of Particle Fouling in Membrane Processes

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1. Introduction

Understanding of fouling in membrane filtration processes is compounded by the variety of substances subjected to these processes. The constituents in the feed streams can comprise particulates, colloids (submicron particles), biological materials, organic matter, proteins, and various dissolved inorganic materials, which can either individually or acting in concert, foul the membrane[1,6,23,50]. It is governed by several physical and chemical factors, not all of which are well understood. Furthermore, the interplay between these physico-chemical phenomena in different types of membrane modules[51,52] exacerbates the problem of understanding the fouling phenomenon. Consequently, most of the earlier theoretical treatments of membrane fouling are strongly biased by empirical models.

Sound theoretical tools for understanding the fouling behavior in membrane filtration processes can lead to successful means for abatement of flux decline resulting from fouling[1]. The present review aims to provide a concise description of the available theoretical techniques for modeling colloidal membrane fouling, their applications and limitations, and future directions in research on membrane fouling. As most large-scale MF and UF plants operate with rectangular or tubular crossflow modules at low operating pressures[39,51,52],

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the review will primarily focus on models addressing such systems. Three major modes of colloidal fouling will be reviewed, including cake formation, pore blocking, and adsorption, with major emphasis on fouling due to cake formation, as this is the dominant mode of fouling in colloidal systems. The study will focus on identifying prior research that has led to a systematic development of our theoretical understanding of fouling based on a comprehensive microscopic picture of the interplay between various physical and chemical phenomena occurring in colloidal systems during membrane filtration processes.

2. Classification of Membrane Fouling

Some of the most common causes of fouling include deposition of a cake layer[1,15,17,53-58], pore blocking[33,57,59-63], particle adsorption[22,23,25,30,31, 64-68], and scaling[9,69-71]. Amongst these, cake formation is perhaps the most dominant mode of long term membrane fouling[1,72]. Based on kinetic models of adsorption or pore blocking, it is generally observed that fouling by these processes is rapid, and is jointly responsible with concentration polarization for the rapid initial flux decline[64,72]. Apart from this, there is a considerable doubt regarding the actual mechanism of protein or macromolecular fouling in UF and MF processes, in which the macromolecular species are known to foul the membranes by adsorption as well as by formation of a cake layer[4,23,25,64]. In this review,

$\sigma << d_p$ $\sigma \sim d_p$ $\sigma >> d_p$

Adsorption   Pore Blocking   Deposition/
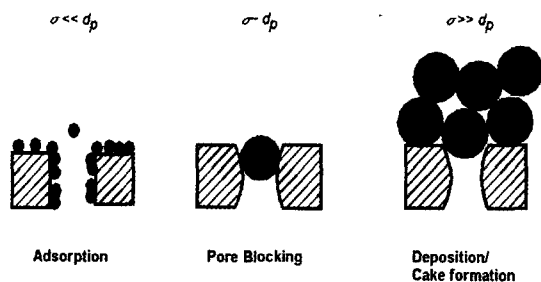   Cake formation

Fig. 1. Different modes of membrane fouling predominantly observed in microfiltration processes.

we will focus only on fouling by cake formation, pore blocking, and adsorption. Scaling and other modes of fouling (for instance, biofouling) are beyond the scope of the present review primarily because scaling is not caused by colloidal materials, while biofouling is caused by interaction of the membranes with living matter, which have different dynamics than colloidal fouling.

A qualitative description of various modes of colloidal membrane fouling can be derived from a consideration of the relative sizes of the membrane pore (diameter, d_p) and the colloidal particle (diameter, σ)[1]. Depending on whether the colloidal particles are smaller or larger than the characteristic pore dimensions of the membrane, one can easily rule out certain possibilities. For instance, if the colloidal particles are larger than the pore size, the particles cannot enter the pores, and consequently the only modes of fouling will be limited to the surface of the membrane in contact with the feed solution. In contrast, when the particles enter the pores, there are possibilities of additional modes of fouling to come into play, including physical blocking of pores and adsorption of particles to the pore walls. Figure 1 schematically describes the classification of various colloidal fouling mechanisms. In most membrane filtration operations, the mean membrane pore diameter is selected in such a way, that most of the particles to be separated are larger than the pore size. However, due to the inherent broad distribution of pore sizes in commercial membranes[24,73,74], intrusion of particles into the membrane matrix cannot be completely ruled out. Consequently, the extent of fouling

due to pore blocking and adsorption also needs to be addressed in practical operations.

An important contrast between fouling by cake formation and the other two modes is the reversibility of the former[34,75-77]. Generally, the deposition of particles can be minimized during operation by adjusting the crossflow velocity and other operating conditions [45,78-80]. Furthermore, washing the membranes can result in removal of almost the entire cake deposit, thereby recovering the flux decline due to cake deposition. On the other hand, fouling by pore blocking or adsorption is generally irreversible, and can be partially removed only by back-flushing the membrane [81] or aggressive chemical cleaning.

2.1. Cake Layer Deposition

For particles that are considerably larger than the pore dimensions, the principal mechanism of separation is sieving at the membrane surface. The retained particles deposit on the membrane forming a cake (or gel) layer. The growing cake layer offers additional resistance to solvent flow, causing a decline in permeate flux. For dead end filtration processes, the cake layer grows indefinitely[82], while during crossflow filtration, the growth of the cake layer is limited by the tangential fluid flow in the module[83-85]. Traditional models of membrane fouling due to cake layer growth predominantly focus on the dead-end configuration, and are not easily scalable to crossflow operations[82]. Modern theories are considerably more effective in addressing the various mechanisms of hydrodynamic and other physico-chemical interactions that limit the growth of a cake layer in crossflow modules [1].

A schematic of the cake layer deposition and the ensuing permeate flux decline in a crossflow filtration process is depicted in Figure 2. During typical crossflow filtration processes, the rejected particles accumulate at the membrane surface, thereby increasing the particle concentration in this region. The concentration gradient induces a diffusive flux of solute particles
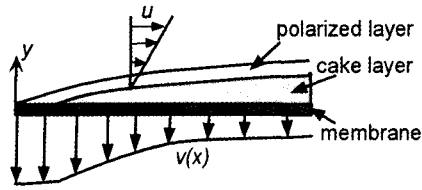
Fig. 2. A schematic of a crossflow MF process showing the development of the cake layer and the corresponding permeate flux decline along the axial direction.

toward the bulk solution. In suspensions of large colloidal particles, the diffusive mobility is generally quite small compared to the permeation drag directed towards the membrane, and the accumulation of particles is quite severe. This results in a rapid attainment of a close packed structure of the particles at the membrane surface that tends to separate as a cake layer. The axial flow of the bulk solution (denoted by u) can, however, result in several modes of removal of particles from the cake layer[1,5,83,86-89]. These modes include shear induced particle lift, inertial lift, and shear induced diffusion. Such models of particle transfer have been proposed to account for the "flux-paradox" generally encountered in colloidal systems and have been reviewed extensively[1,90]. Although such mechanisms gained importance during the past decade, it has been realized that such mechanisms are appropriate for large non-Brownian particles > 1 μm [90]. It should be noted that the axial velocity profile is drawn from the cake surface in Figure 2, signifying a stationary (immobile) cake layer. There are instances, however, where the cake layer itself or parts thereof can move along the filtration channel. Treatments of such mobile cake layers have received increased attention during the recent years[58,88,91,92].

Apart from the purely hydrodynamic interactions, there may be several chemical interactions that govern the structure, rigidity, and permeability of the cake layer. Such interactions can be expressed in terms of appropriate mathematical relations for the particle-membrane and particle-particle affinity or repulsion [90,93-95]. The physical and chemical forces acting on the individual particles in a cake layer govern the

tendency of these particles to remain in the cake layer, or become re-entrained in the bulk solution.

2.2. Pore Blocking

Pore blocking is important in the initial stages of microfiltration, particularly those using "leaky" membranes. The situation arises when colloidal or particulate materials enter the pores and get trapped in the constrictions within the membrane matrix. The physical blocking of the pores prevents further transport of solvent through the affected pores, resulting in a reduction in permeate flux. Pore blocking is generally observed when using commercial membranes with a broad pore size distribution. As the solvent velocity across a pore depends on the 4th power of the pore radius, larger pores are responsible for a major fraction of the permeate seepage across a membrane. However, the solute particles that are entrained in the membrane matrix, will quickly block these large pores and lower the overall permeate flux. The phenomenon occurs rapidly in the initial stages of the filtration process, and may continue for a longer duration in certain isolated instances using very small colloidal particles or a polydisperse suspension[1]. Pore blocking has been primarily modeled using various semi-empirical approaches, notably those employing the blocking laws proposed by Hermia[60]. Modern studies tend to employ exponential decay models for flux decline due to pore blocking to account for the rapid initial flux decline[64,72].

2.3. Adsorption

Adsorption of particles on the surface and the pore walls of a membrane results from chemical interactions between these particles and the membrane material[23,25,30,31]. The adsorbed particles lower the effective pore diameter of a membrane causing a reduction in the permeate flux and an enhancement in solute particle rejection[25,64]. Adsorption phenomena usually occur during the initial stages of membrane filtration, as the modification of the surface properties of the adsorbed membrane surface will prevent further attach-

ment of particles. Adsorption generally leads to irreversible loss in permeability of the membrane and can be removed only by some form of chemical cleaning. UF and MF applications in food and biomedical separations encounter severe fouling due to protein adsorption[25,96]. In wastewater treatment, humic substances (natural organic matter, NOM) are also known to adsorb on hydrophobic membranes[31].

3. Models of Colloidal Fouling

Modeling of permeate flux decline has been addressed extensively during the past three decades starting from the studies of Blatt *et al*.[97]. The original dichotomy of the theoretical approaches, namely, whether permeate flux decline can be addressed from a purely thermodynamic (osmotic pressure model) or hydrodynamic (filtration theory) viewpoint, has been the subject of several studies[82,98-103]. The dichotomy of the theoretical approaches has been reviewed comprehensively[1,90,104]. The outcomes of these studies have ranged from development of semi-empirical resistance in series type models[105,106] to the gradual acceptance of a unified view of the entire gamut of membrane filtration processes[92,102,103,107,108]. It has long been recognized that traditional approaches based on osmotic pressure or filtration models, or even the resistance in series models, can only be used to correlate experimental observations, but are not suitable for prediction of permeate flux or the extent of fouling. This has led to a systematic development of theoretical models that attempt to present an accurate microscopic (particle level) description of the physico-chemical phenomena in the polarized and cake layers and their influence on the cake structure, porosity, and permeate flux decline.

There are two major issues pertaining to fouling due to cake deposition, namely, identification of the causes of cake formation, and determination of the cake layer properties and the dynamics of cake growth. The former has rarely been addressed in membrane re-

search. Ideally, a cake layer should be formed when a colloidal dispersion attains a certain concentration (more specifically, a particle volume fraction) above which the colloidal particles spontaneously phase-separate to form coexisting solid and liquid phases[107,109,110]. Curiously, the theoretical advancements that address the mechanisms of phase separation in colloidal systems, for instance, theories of sedimentation or disorder-order transition in colloidal dispersions[109], have been inducted in the studies of membrane filtration processes only during the past few years[110-112]. However, once incorporated in the framework of membrane filtration models, these additional insights might lead to a clearer perception of the thermodynamic and hydrodynamic factors governing cake formation.

The conditions under which a colloidal dispersion undergoes a transition from a disordered state to an ordered cake-like structure is still a matter of conjecture since detailed theories for concentrated colloidal dispersions are in a very immature state[109]. For hard spherical particles such transitions are expected to occur at particle volume fractions 0.64 to 0.72 giving rise to either a random close packed or a hexagonal close packed cake structure[93,107,109]. In charged systems, such phase transitions may occur at even lower particle volume fractions[109]. However, phase transition mechanisms leading to cake formation are relatively important only for very small colloidal or macromolecular particles (diameter < 100 nm) where the thermodynamic contributions are significant enough to retain the colloidal particles in a dispersed (liquid-like) state. For larger particles, the thermodynamic forces become insignificant, and the colloidal dispersions may separate into coexisting liquid and solid phases almost spontaneously under the influence of gravity. Thus, during MF of large particulate suspensions, the cake layer formation initiates almost instantaneously[72].

The dynamics of cake layer growth and evaluation of the cake layer properties, like structure and permeability, have received considerably greater attention over the recent years. There has been a significant
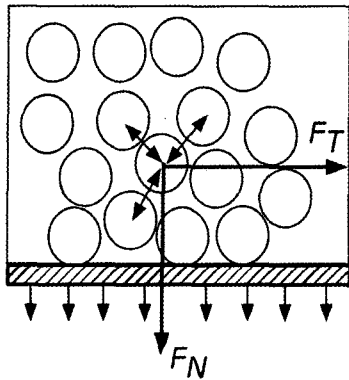
Fig. 3. Forces acting on a particle in a cake layer.

resurgence of studies that attempt to directly incorporate colloidal interactions in predicting the structure and permeability of the cake layer deposits. Such studies were pioneered by a set of experimental observations by McDonogh et al.[113]. Further studies were pursued to assess the influence of particle charge, background electrolyte concentration, and other physicochemical conditions on the permeability of the filter cake[50,114,115]. There have been a variety of studies pertaining to elucidation of the structure of the cake layer under the influence of colloidal and hydrodynamic interactions, some even involving computer simulations[95].

3.1. Mechanistic Description of the Physico-Chemical Phenomena at a Membrane Surface

The primary focus in the modern theoretical developments is the identification of the predominant forces that engender particle deposition on membrane surfaces leading to cake layer growth[95,116]. In typical crossflow filtration modules, the various forces acting on the colloidal particles near the membrane can be resolved into two components acting tangentially and vertically (depicted schematically in Figure 3). The individual force components arise due to the hydrodynamic interactions resulting from the relative motion of the solvent with respect to the colloidal particle [107,116], and various thermodynamic forces resulting from chemical potential gradients and interparticle or

particle-membrane interactions[95,110]. The sum of all these forces dictates the propensity of a particle to deposit on the membrane as a stationary cake layer.

It is straightforward to identify two components of the hydrodynamic forces, namely, a normal component owing to the permeation drag, and a tangential component arising from the crossflow. While the normal permeation drag force tends to bring the particles closer to the membrane surface, the tangential force can be manifested as inertial and lift forces that tend to lift the particles form the cake. However, when a particle is lodged in an immobile cake layer, the tangential force due to the crossflow becomes insignificant except possibly at the cake surface. Gravitational forces may also come into play, acting normal to the membrane. It is, however, known that gravitational forces are insignificant for particles smaller than ~ 10 μm[95]. Finally, the Brownian forces on the particles result in a diffusive movement of the particles from the cake to the bulk solution[90,110]. The Brownian force is important for small colloidal particles, and is aided by the concentration gradient between the cake layer and the bulk solution. Nearly all the forces are particle size dependent, and typical magnitudes of these forces are shown in Figure 4 as a function of particle diameter corresponding to a permeate flux of 2 $\times$ 10^{-5} m/s. It is apparent that gravity and inertial forces are quite negligible in membrane filtration processes involving colloidal particles in the size range of 10 nm$\sim$300 nm, and the cake layer buildup is primarily governed by the interplay between the permeation drag, Brownian forces, and the interparticle interactions[93,95,103,107,116].

3.2. Colloidal Interactions

The Derjaguin-Lanadu-Verwey-Overbeek (DLVO) potential is commonly used to determine the colloidal interactions between the particles[109]. This interaction potential comprises an attractive van der Waals and an electrostatic double layer component, which is repulsive for similarly charged particles. The magnitudes of
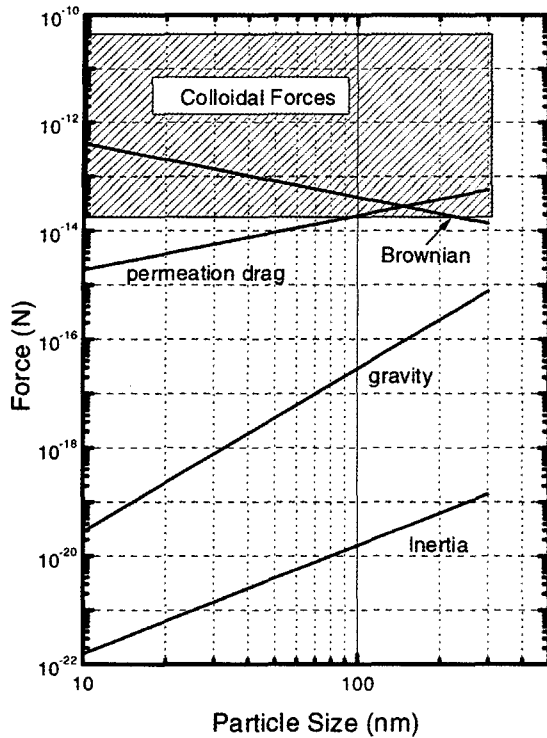
Fig. 4. Typical magnitudes of different physico-chemical forces acting on a colloidal particle during membrane filtration. Gravity and inertial effects are negligible for submicron particles. Consequently, the structure of the cake layer is governed primarily by the permeation drag, Brownian, and colloidal forces. The colloidal forces are dictated by the interparticle separation, solution ionic strength, particle charge, and the Hamaker constant. All other forces are governed mainly by the particle size.

both these interactions increase with increasing particle size. However, the magnitude and range of the DLVO interaction potential is strongly affected by the background electrolyte concentration and the particle surface charge. It is worth noting that the DLVO potential gives the interaction energy and force between two isolated colloidal particles (an effective pair potential). Calculation of potentials and forces in a concentrated system involves accounting for the many body effects, which is generally performed using pairwise summation of the binary interactions[93,110,112]. It is at this juncture, that the structure of the dispersion or the cake layer comes into play. The net colloidal interaction force acting on a particle will depend on the

positions of the neighboring particles. A colloidal system will generally tend to attain an equilibrium structure, which minimizes the total repulsive energy between the particles. Both entropic and energetic considerations are essential in relating the structure to the interaction potentials[110,112].

The typical range of colloidal forces between two colloidal particles in a cake layer is depicted in Figure 4. The magnitude of the force depends on the separation distance between the particles. For a given interparticle separation, it is possible to vary the force by at least one order of magnitude by adjusting the ionic strength of the solution and the particle surface charge[109]. This feature has implications in manipulation of solution properties to yield cake layers of different permeability and thickness. Furthermore, variation of solution ionic strength can also result in aggregation of the colloids (at high ionic strengths) resulting in larger flocs, which deposit on the membrane to form a more permeable cake layer[109,117,118].

Adding polyelectrolytes or surfactants can also manipulate the range and magnitude of the colloidal interactions[119,120]. It is possible to induce attractive depletion forces between the colloidal particles at any ionic strength by adding suitable polyelectrolytes and produce larger particles in the cake layer by coagulation[109].

The possibility of tailoring the cake layer properties by changing the composition of the feed solution (through appropriate feed pre-treatments) is an attractive option in controlling membrane fouling, and is being pursued vigorously by several researchers.

3.3. Hydrodynamic Interactions

One of the major hydrodynamic forces acting on the particles near the membrane is the permeation drag arising from the friction between the solvent and the retained particles[116]. In a dilute system this friction is represented by the classical Stokes friction factor [109]. However, in a concentrated system, the hydrodynamic interactions are considerably modified due

to the presence of the neighboring particles. Incorporating the influence of the neighboring particles on the hydrodynamic drag force can be achieved through Happel's cell model[55,121], or through statistical mechanical procedures that employ pairwise summation of the hydrodynamic interaction parameters based on Stokes solution for the hydrodynamic interaction between two particles. Happel's approach is known to yield the correct limiting behavior for highly concentrated cake-like systems, and has often been suggested as a substitute for the Kozeny-Carman equation for evaluating the specific resistance of cake layers. The statistical mechanical approaches are, on the other hand, more appropriate for dilute systems yielding the correct asymptotic values of the hydrodynamic drag forces in the infinite dilution limit. Embedded in both the cell model and the statistical mechanical approach are the structural information about the particle layer. These procedures of evaluating the hydrodynamic interactions provide the total frictional drag per unit thickness of a cake layer, and can also be employed to evaluate the total pressure drop across a concentration polarization layer with variable particle volume fraction. These techniques can be used to determine the sedimentation coefficient and the gradient diffusion coefficient of the colloidal particles in a polarized layer, and form a basis of the unified approach for modeling flux decline due to the combined effects of concentration polarization and cake formation.

3.4. Concentration Polarization and Cake Formation

Concentration polarization is a precursor of fouling by cake formation. Concentration polarization during crossflow membrane filtration and the ensuing permeate flux decline are generally modeled by coupling the convective-diffusion equation with an appropriate expression governing the permeate transport. This coupled model for concentration polarization and flux decline may be regarded as the cornerstone of our theoretical understanding of membrane filtration in-

volving a diverse array of colloidal and macromolecular systems[90,98,103,104].

The above macroscopic continuum model, even in its most general formulation, often fails to provide a complete theoretical perspective of the flux decline behavior. This limitation is apparent from the inability of the model to accurately and independently predict the permeate flux behavior for a wide range of solutes. The shortcomings of the theory have often been ascribed to the use of inappropriate expressions for transmembrane permeate transport. Rather indiscriminate use of the thermodynamic (osmotic pressure model) and hydrodynamic (filtration theory) approaches to model the transmembrane transport led to considerable confusion regarding the actual mechanism of concentration polarization and flux decline during the past two decades[90,98,99,104]. However, it gradually became transparent that these two approaches might be equivalent, particularly when modeling the concentration polarization phenomenon of solute particles in the absence of a cake layer buildup[105,110]. Recently, it was shown that the osmotic pressure and filtration (hydrodynamic) approaches constitute equivalent alternative descriptions of the concentration polarization phenomenon[103,107]. Despite these advancements, however, *a priori* predictions of permeate flux based on solution and membrane properties still remain elusive to a large extent.

The inability of the convective-diffusion model to predict the permeate flux accurately may also be ascribed to the absence of any information regarding the physico-chemical interactions between the solute particles in the model framework. Two parameters in the convective-diffusion model, namely, the osmotic pressure and the gradient (mutual) diffusion coefficient, are generally supplied in the form of experimental correlations or are used as adjustable parameters[100,102,104-106,122]. Embedded in these two macroscopic properties is an astounding amount of information regarding the physico-chemical interactions between the solute particles in the polarized layer and

the solution structure engendered by such interactions. Use of experimental correlations for concentration dependence of osmotic pressure or empirical values of diffusion coefficient does not provide a quantitative understanding of these interparticle interactions. The paucity of a sound theoretical link between these macroscopic properties and the interparticle interactions often renders the convective-diffusion model of flux decline semi-empirical, capable only of fitting experimental data using adjustable parameters.

A comprehensive predictive theory of flux decline should relate the physico-chemical interactions between the solute particles in the polarized layer to the osmotic pressure and the diffusion coefficient. The resulting estimates of diffusion coefficient and osmotic pressure, when substituted in the flux decline model, may render the macroscopic model capable of quantifying the influence of interparticle interactions on permeate flux decline. Incorporation of interparticle interactions in models of flux decline has received considerable attention over the recent years[50,90,93,94,96,113-115, 123,124]. The first quantitative incorporation of interparticle interactions to investigate permeate flux decline behavior was motivated by experimental observations of the effect of particle charge, solution pH, and ionic strength on the permeate flux[96,113-115]. Bowen and Jenner[90] have comprehensively reviewed most of these earlier investigations. More recent studies on the influence of solute-solute interactions[93,94,111,124] are generally based on cell models (For instance, [121, 125]). Most of these studies assume a fixed structure for the concentration polarization layer while computing the interactions. Such a priori assumption of the solution structure may be reasonably accurate for systems where a cake layer has formed, but is inadequate for a disordered liquid-like system[126] typically represented by a concentration polarization layer.

The above limitation of the cell models may be overcome by employing rigorous statistical mechanical theories to relate the interparticle interactions to the structure of the solution (dispersion)[109,126-128]. Con-

trary to the cell models that assume a fixed geometrical structure of the cake layer, the statistical mechanical approach allows the interparticle interactions to dictate the structure of the solution. This feature makes the approach amenable for studying the structure and thermodynamic properties of concentrated disordered systems. Furthermore, such procedures may be used to predict the disorder to order transition point in the colloidal systems that leads to the onset of cake formation.

A substantial theoretical development has been made in the understanding of sedimentation and gradient diffusion using statistical mechanical procedures[109, 126-128]. Noting that the dispersion microstructure evolves from the interparticle and hydrodynamic interactions in essentially the same manner during sedimentation and membrane filtration processes, the theory of batch sedimentation may be extended to predict permeate flux decline in membrane separation processes [109]. However, the statistical mechanical theory of sedimentation is reasonably accurate only for dilute monodisperse suspensions of hard-spherical particles [126]. Till date there have been very limited studies on the influence of long-range interparticle colloidal interactions at higher solute particle concentrations based on this approach[110,129].

It was recently shown that incorporation of the concentration dependent gradient diffusion coefficient in the convective diffusion equation can lead to predictions of filtration behavior that are qualitatively and quantitatively different from the predictions based on a constant diffusivity. In repulsive colloidal systems, the incorporation of variable diffusivity results in a dramatic lowering of the concentration polarization, and hence, an increase in the permeate flux. This implies that the cake formation is initiated in charged colloidal systems at significantly higher pressures than those predicted by a constant diffusivity model. Such studies for the basis of further exploration of the cake formation mechanisms, their dependence on operating conditions and solution properties, and finally, addressing the "flux-paradox" in membrane filtration processes in a

3.5. Dependence of Cake Growth on Operating and Physico-Chemical Conditions

The extent of membrane fouling is affected by the operating conditions, such as the applied pressure[16, 59,130], the crossflow velocity of the feed solution [29,131,132], and the feed concentration[97,133,134]. Amongst the different physical parameters governing the extent of fouling, perhaps the most important is the applied pressure difference which governs the initial permeation rate. It has long been recognized that low-pressure microfiltration is much more effective than high-pressure microfiltration. It has become quite clear over the past decade that membrane fouling is severely enhanced at higher applied pressures[20, 45,135-137]. Thus, although at higher operating pressures the initial permeate flux is high, there is a rapid decline in the flux, and in certain instances, increasing the operating pressure results in a lower limiting permeate flux[138]. The pressure independence of the limiting flux was observed in some of the earliest experimental studies on ultrafiltration[97]. Such phenomena were analyzed in light of cake filtration theory [139], where it was proposed that the cake layer was compressible[140], and the enhanced resistance of the compressed cake layer compensated for the increased pressure induced driving force[138,139,141].

This strong dependence of fouling propensity on applied pressure led to considerable amount of studies aimed toward identification of a critical pressure below which there will be no or negligible fouling[16,59,137, 138,142-146]. Most of these studies were performed in microfiltration or ultrafiltration processes involving microporous membranes and, consequently, higher initial permeation rates compared to nanofiltration or reverse osmosis membranes. The critical-flux hypothesis is based on the premise that on start-up there exists a flux below which a decline of flux with time does not occur. In some cases, constant-flux filtration was realized at a constant transmembrane pressure, which was below a critical value[16]. In general, constant-flux filtration was obtained with moderately increasing transmembrane pressure, and this approach has some advantages over normal constant-pressure filtration because it clearly provides for the possibility of avoiding over-fouling and reduces the severity of fouling.

The critical flux of the membranes is also dependent on the crossflow velocity. The higher the flow velocity, the higher the pressure that could be used without a decrease in permeate flux[147]. A recent study[58] presents observations of particle deposition on microfiltration membrane surfaces using a non-invasive, in situ, continuous direct observation through the membrane (DOTM) technique. The filtration tests were conducted in the imposed flux mode, so that the flux could be controlled at, below, or above the critical flux. Below the critical flux, the particle deposition was negligible; near the critical flux the particle deposition was significant; and above the critical flux, particle layers were formed on the membrane surface. It was further observed that the particle size distribution of the deposited particles changed with the crossflow velocity, with smaller particles deposited on the membrane at higher crossflow velocity.

The critical flux concept introduced by Field et al. [16] was verified recently in a membrane bioreactor as a means of achieving the critical operating conditions required for optimal performance[45]. Experiments were conducted on a membrane bioreactor containing activated sludge, equipped with a ceramic membrane. Two series of tests were conducted: at fixed transmembrane pressure (TMP) and at fixed permeate flux. In both cases, the crossflow velocity was varied. In fixed flux tests, the flux was increased by small increments and the TMP was observed to rise moderately first and then stabilize within a short interval until a critical value of the flux is reached. Above this critical flux, the TMP rises rapidly and does not stabilize, as in dead-end filtration.

The critical flux was found to increase approxi-

mately linearly with crossflow velocity. Comparison of constant pressure and constant flux tests under same conditions showed that the critical flux is almost identical to the limiting or pressure independent flux obtained in constant pressure. More generally, constant flux procedure below the critical flux avoids over-fouling of the membrane in the initial stage. It is apparent that the physico-chemical properties of the suspension, for instance, the particle charge and the solution electrolyte concentration[50,108,148], would act in conjunction with the operating pressure to dictate the critical flux. The effect of particle size and ionic strength of the feed suspension on critical flux was studied recently[149], and both these factors were found to significantly affect the extent of fouling. It was observed that the ionic strength of suspension had significant effect on the critical flux. For low ionic strengths there was a decrease in the critical flux. It was suggested that this could be due to the dense layer of deposit comprising smaller colloidal particles. At higher ionic strengths, a significant increase in critical flux was noticed which may be due to the aggregation of particles, resulting in larger flocs and hence a more porous cake layer deposit.

It is, however, imperative to note that the influence of background electrolyte concentration on the propensity of colloidal fouling of NF or RO membranes should be significantly different from those observed in UF or MF processes. The "tighter" membranes in RO or NF are capable of rejecting the small ionic species, which would result in concentration polarization of these ions near the membrane[150]. Consequently, irrespective of the bulk feed concentration of these ions, there would always be a high electrolyte concentration near the membrane surface in these processes. Therefore, the particle-membrane and particle-particle electrostatic repulsion will be considerably short ranged near the membrane surface due to the screening effects of the electrolyte. This can significantly affect the extent of colloidal fouling and the critical flux in NF and RO processes. Such com-

plexities do not arise in MF or UF membranes, which do not reject the ionic species, and it suffices to consider the bulk electrolyte concentration when calculating the electrostatic double layer interactions in the cake layer[93,108,145,149].

Although a critical flux is difficult to predict without a sound theoretical understanding of the underlying physico-chemical phenomena, there have been recent efforts to pinpoint this flux through bench scale experiments and scale up these results to identify the operating conditions in actual plants that would minimize fouling[151,152]. Similar emphasis on experimental determination of the critical flux is indicated in other studies[58,137].

4. Summary

The permeate flux decline due to membrane fouling can be addressed using a variety of theoretical standpoints. Judicious selection of an appropriate theory is a key toward successful prediction of the permeate flux. The essential criterion for such a decision appears to be a detailed characterization of the feed solution and membrane properties. Modern theories are capable of accurately predicting several properties of colloidal systems that are important in membrane separation processes from fundamental information pertaining to the particle size, charge, and solution ionic strength. Based on such information, it is relatively straightforward to determine the properties of the concentrated colloidal dispersion in a polarized layer or the cake layer properties. Incorporation of such information in the framework of the standard theories of membrane filtration, namely, the convective diffusion equation coupled with an appropriate permeate transport model, can lead to reasonably accurate prediction of the permeate flux due to colloidal fouling. The schematic of the essential approach has been delineated in Figure 5.

The modern approaches based on appropriate cell models appear to predict the permeate flux behavior in crossflow membrane filtration processes quite accurately
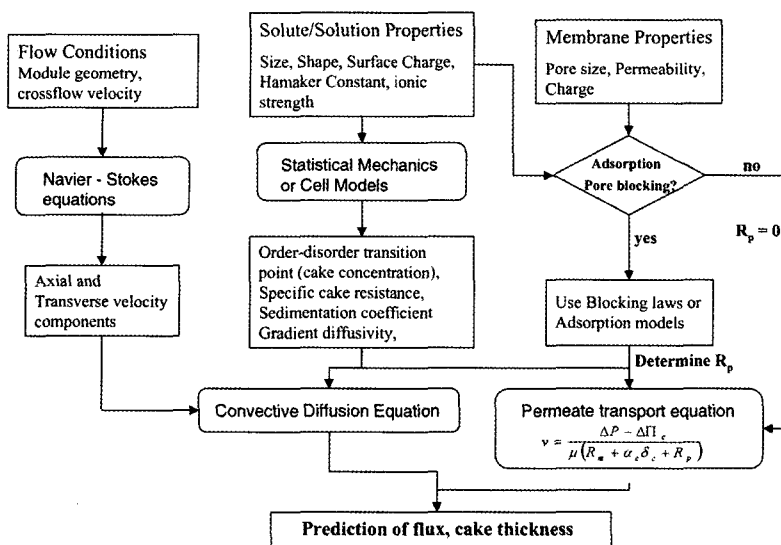
Fig. 5. Flowchart depicting a general methodology of predicting the extent of permeate flux decline due to colloidal fouling. Here, R_p is the resistance due to pore blocking and adsorption, α_c is the specific resistance of the cake layer, δ_c is the cake layer thickness, and $\Delta \Pi_c$ is the transmembrane osmotic pressure difference.

without invoking novel theoretical descriptions of particle back transport mechanisms or depending on adjustable parameters. Such agreements have been observed for a wide range of particle size ranging from small proteins like BSA (diameter ~ 6 nm) to latex suspensions (diameter ~ 1 μm).

There are, however, several areas that need further exploration. Some of these include:

1) A clear mechanistic description of the cake formation mechanisms that clearly identifies the disorder to order transition point in different colloidal systems.

2) Determining the structure of a cake layer based on the interparticle and hydrodynamic interactions instead of assuming a fixed geometrical structure on the basis of cell models.

3) Performing well controlled experiments where the cake deposition mechanism can be observed for small colloidal particles (< 1 μm).

4) A clear mechanistic description of the critical operating conditions (for instance, critical pressure) which can minimize the propensity of colloidal membrane fouling.

5) Developing theoretical approaches to account for polydisperse systems that can render the models capable

of handing realistic feed solutions typically encountered in diverse applications of membrane filtration.

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