Factors Affecting Flux Decline in Crossflow Membrane Filtration of Particulate Suspensions

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Abstract

Series of well-controlled membrane filtration experiments are performed to systematically investigate the dynamic behavior of permeate flux in crossflow membrane filtration of colloidal suspensions. Results are analyzed by a transient permeate flux model which includes an approximate closed-form analytical expression for the change of permeate flux with time. The model is based on a simplified particle mass balance for the early stages of crossflow filtration before a steady state flux is attained, and Happels cell model for the hydraulic resistance of the formed particle cake layer. The filtration experiments demonstrate that permeate flux declines faster with increasing feed particle concentration and transmembrane pressure. It is also shown that crossflow velocity (shear rate) has no effect on the permeate flux at the transient stages of crossflow filtration. Pressure relaxation experiments indicate that the particle cake layer is reversible, implying no irreversible deposition (attachment) of particles to the membrane surface or to accumulated (retained) particles. Experimental observations also showed that permeate flux decline rate increases as the ionic strength of the feed suspension increases, indicating that colloidal interactions have a significant influence on permeate flux decline.

Keywords: membrane filtration, transient permeates flux model, colloidal interactions

1. Introduction

Pressure-driven membrane filtration, such as microfiltration (MF) and ultrafiltration (UF), is an essential separation process in numerous fields of industries [Kelly and Zydney, 1995; Marshall et al., 1991; Fane, 1986]. Membrane filtration has proved to be very effective for removal of organic, inorganic, and biological

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The manuscript for this paper was submitted for review on June 8, 1998.
colloids from various processing waters [Adham et al., 1996; Belfort et al., 1994]. In particular, the use of membranes in the water treatment industry is expected to increase even more due to stringent current and pending drinking water regulations such as Surface Water Treatment Rule (SWTR) [Adham et al., 1995].

The application of membrane filtration is, however, restricted by a gradual decline in permeate flux over time due to accumulation of rejected colloidal particles on the membrane surface [Barger and Carnahan, 1991; Zhu and Elimelech, 1995; AWWA committee, 1992; Potts et al., 1981]. Most process waters contain a variety of colloidal particles including metal oxides, clays, macromolecules, and biocolloids such as bacteria. These colloidal particles are not completely removed by typical pretreatment processes, and thus reduce the efficiency of membrane systems.

Permeate flux decline in membrane filtration of colloidal suspensions may be characterized by two processes: short-term flux decline due to concentration polarization and cake formation, and long-term flux decline due to fouling and cake compaction [Davis, 1992]. As soon as transmembrane pressure is imposed, colloidal particles move toward the membrane surface and accumulate near the membrane surface. The buildup of particle concentration in the vicinity of the membrane surface, typically known as concentration polarization, leads to the formation of the particle cake layer [Song and Elimelech, 1995b]. The cake layer acts as an additional resistance to permeate flow and causes a rapid permeate flux decline, generally occurring on the order of minutes or hours. Permeate flux further decreases slowly over time (i.e. in scale of hours or days) because of the consolidation of the cake layer. Membrane fouling, generally referred to as a reduction in membrane permeability due to irreversible particle adsorption within membrane pore or to the membrane surface, also contributes to long-term permeate flux decline [Chellam and Wiesner, 1992; Lepore and Ahlert, 1988].

Fundamental understanding of transient permeate flux behavior is of paramount importance for designing membrane systems and determining the cleaning frequency [Romero and Davis, 1990]. Unfortunately, most of theoretical efforts have been devoted to development of steady-state flux models [Bowen and Jenner, 1995a; Belfort et al., 1994]. Transient flux models regarding membrane filtration of colloidal suspensions are relatively limited. Furthermore, the majority of existing models are rather empirical, requiring experimentally determined or adjustable fitting parameters [Fane, 1986].

The most popular theory for membrane filtration dynamics is the hydraulic resistance in series model [Bowen and Jenner, 1995]. This model, originated from the classical filtration theory [Hlavacek and Bouchet, 1993; Hermia, 1982], incorporates various water flux decline mechanisms by introducing them as separate hydraulic resistances into Darcy's equation [Tracey and Davis, 1994; Viswanathan and Ben Aim, 1989].

Furthermore, each resistance is often assumed to be time-dependent to accommodate variations in resistances over time, such as membrane compaction and cake layer consolidation [Bhattacharjee et al., 1996; Davis, 1992]. This model offers a simple but convenient tool to fit experimental results. However, the model does not provide a fundamental theoretical basis for each hydraulic resistance.

The application of transient models is generally restricted to dead-end filtration, although existing models may be modi-
fied for the crossflow filtration by introducing empirical parameters. Unlike dead-end filtration, the extent of permeate flux decline in crossflow filtration is limited by shear flow and a steady-state flux is ultimately achieved [Davis, 1992; Mackley and Sherman, 1992]. Numerous models describing the steady-state flux in crossflow membrane filtration of colloidal suspensions have been developed by incorporating additional shear-induced mass transfer mechanisms [Davis, 1992; Lojkine et al., 1992].

Representative examples include inertial migration [Drew et al., 1991; Altena and Belfort, 1984; Green and Belfort, 1980], shear-enhanced diffusion [Romero and Davis, 1988; Zydney and Colton, 1986], and shear-induced convection [Vassilieff, 1992; Leonard and Vassilieff, 1984]. Recently, Song and Elimelech [1995b] have developed a novel model describing crossflow filtration of colloidal suspensions based on hydrodynamics and thermodynamics of colloidal suspensions. These models may be expanded to unsteady-state flux models by adding suitable transient terms. For instance, Romero and Davis [1990; 1991] derived a transient flux equation for the shear-enhanced diffusion model using the method of characteristics.

In this paper, a series of crossflow membrane filtration experiments are performed with model colloidal suspensions to systematically investigate the effect of physical operating parameters—particle concentration, transmembrane pressure, and crossflow velocity (shear)—on the kinetics of permeate flux decline. The obtained results are compared with theoretical predictions by an approximate transient flux model developed on the basis of hydrodynamics and thermodynamics of colloidal suspensions. In addition, the role of colloidal interactions in crossflow membrane filtration of colloidal suspensions is studied under various hydrodynamic conditions. Lastly, the validity of the approximate model is examined and discussed.

2. Theoretical

2.1 Pressure Drop and Cake Formation

In typical pressure-driven crossflow membrane filtration systems (e.g. spiral wound and hollow fiber), colloidal particles are transported to the membrane surface due to the convective permeate flow induced by the pressure gradient across the membrane. Assuming complete retention of colloidal particles by the membrane, colloidal particles accumulate near the membrane surface and form a concentration-polarization (CP) boundary layer [Denisov, 1994]. The accumulated particles in the CP layer are swept away from the membrane surface and transported toward the exit of the membrane module by the convective crossflow. As particle accumulation continues, particle concentration near the membrane surface reaches its maximum value—typically a random packing density (0.64 v/v)—due to the finite size of particles, and as a result, a particle cake layer starts to form above the membrane surface [Belfort et al., 1994; Davis, 1992]. Further particle transport to the membrane surface results in the growth of the cake layer. The extent of particle accumulation is strongly dependent on the hydrodynamics and thermodynamics of the colloidal suspension [Song and Elimelech, 1995b].

Particle accumulation in both CP and cake layers provides an additional resistance to permeate flow and, hence, reduces permeate flux. Resulting pressure drops in the crossflow membrane filtration system can be expressed as
\[ \Delta P = \Delta P_m + \Delta P_s + \Delta P_c \]  

(1)

Eq. (1) states that the applied pressure (\( \Delta P \)) is equal to the sum of the pressure drops across the membrane (\( \Delta P_m \)), CP layer (\( \Delta P_s \)), and cake layer (\( \Delta P_c \)). The pressure drop across the membrane is simply the product of membrane resistance (\( \lambda \)) and permeate flux (\( v_w \)):

\[ \Delta P_m = \lambda v_w \]  

(2)

The pressure drop in the CP layer can be obtained by integration of the frictional drag over the entire CP layer [Song and Elimelech, 1995b]. However, it can be shown that, once a cake layer forms, the pressure drop in the CP layer is maintained at a critical value:

\[ \Delta P_s = \frac{N_{FC} kT}{\frac{4}{3} \pi a_i^3} \]  

(3)

where \( k \) is the Boltzmann constant, \( T \) is the absolute temperature of the colloidal suspension, \( a_i \) is the radius of the colloidal particle, and NFC is the critical filtration number at which the cake layer begins to appear. Detailed description of the filtration number, NFC, is available elsewhere [Song and Elimelech, 1995b].

Since the particle concentration in the cake layer is fixed at a value, usually corresponding to random packing, the pressure drop in the cake layer is obtained by calculating the frictional drag resulting from permeate flowing through the dense layer of the accumulated particles:

\[ \Delta P_c = \frac{kT}{D} A_s(\theta_{max}) v_w M_c \]  

(4)

Here, \( kT/D = 6\pi \mu a_i \) is the frictional drag coefficient obtained from Einstein-Stokes' law, \( D \) is the particle diffusion coefficient, \( A_s(\theta_{max}) \) is a correction function accounting for the effect of neighboring retained particles, and \( M_c \) is the total number of particles (per unit area) accumulated in the cake layer. The correction function, \( A_s \), is generally evaluated from Happel's cell model [Happel, 1958]:

\[ A_s = \frac{1 + \frac{2}{3} \theta^3}{1 - \frac{3}{2} \theta + \frac{3}{2} \theta^3 - \theta^4} \]  

(5)

where \( \theta = (1 - \epsilon)^{1/3} \) is a porosity dependent variable, with \( \epsilon \) being the porosity of the accumulated particles. The total number of accumulated particles, \( M_c \), is related to the cake layer thickness, \( \delta_c \):

\[ M_c = \frac{\theta_{max} - \theta}{\frac{3}{4} \pi a_i^3} \]  

(6)

2.2 Particle Transport and Mass Conservation

Particle transport within the CP layer can be described by the convective-diffusion equation:

\[ \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} = D \frac{\partial^2 C}{\partial y^2} \]  

(7)

where \( u \) and \( v \) are the fluid velocities in the longitudinal (x) and transverse (y) directions, respectively, \( C \) is the particle number concentration, and \( t \) is the filtration time. In Eq. (7), the longitudinal diffusion term is neglected because it is much smaller than the other terms under typical conditions of crossflow filtration. In addition, the accumulated particles in the cake layer are assumed to be immobile, implying that particle transport takes place only in the CP layer. With the following boundary conditions at the inner and outer edges of the CP layer,

\[ \nu C - D \frac{\partial C}{\partial y} \approx 0, \]

\[ C = C_i, \quad v = v_w \text{ at } y = \delta_c, \]  

(8a)

\[ \frac{\partial C}{\partial y} = 0, \quad C = C, \quad v = v_w \text{ at } y = \delta_c + \delta_e, \]  

(8b)

integration of Eq. (7) over the entire CP
layer yields [Davis, 1992]

\[ \frac{d}{dt} \int_{h_i}^{h_e} (C - C_0) \, dy + (C_e - C_0) \frac{d\delta_p}{dt} + \frac{d}{dx} \int_{h_i}^{h_e} u (C - C_0) \, dy = v_w C_0 \]

(9)

Here \( \delta_p \) and \( \delta_e \) are the thicknesses of the CP and cake layers, respectively, \( C_0 \) is the bulk particle number concentration, and \( C_e \) is the particle number concentration in the cake layer. Each term of Eq. (9) (from left to right) represents particle accumulation in the CP layer, particle accumulation in the cake layer, particle convection in the CP layer by crossflow, and particle convection into the CP layer by permeate flow, respectively. At steady state, the first two transient terms vanish and Eq. (9) reduces to

\[ \int_{h_i}^{h_e} u (C - C_0) \, dy = C_0 \int_{0}^{x} v_w \, dx \]

(10)

Eq. (10) implies that, at steady state, particle transport into the CP layer by the permeate flow is balanced by particle transport in the longitudinal direction by the crossflow.

2.3 Approximate Solution for the Transient Permeate Flux

Solving Eq. (9) requires the use of numerical techniques. However, this equation can be simplified based on assumptions reasonably applicable to typical membrane filtration of colloidal suspensions. First, particle accumulation in the CP layer is assumed to reach steady state in a very short time. Many researchers have shown that a steady state in the CP layer is achieved very rapidly, typically on order of minutes depending on hydrodynamic conditions [Fane, 1986]. Second, it is assumed that initial water flux decline is independent of the longitudinal flow. Davis [1992] has indicated that a dead-end filtration theory provides a good approximation to describe permeate flux decline at the initial stages of membrane filtration, implying that the crossflow has only a little effect on permeate flux reduction. Based on the above two assumptions, the first and third terms in Eq. (9) vanish and the following simple particle mass balance equation is obtained:

\[ (C_e - C_0) \frac{d\delta_e}{dt} = v_w C_0 \]

(11)

In fact, Eq. (11) is identical to the mass conservation equation for dead-end filtration.

In typical membrane filtration of colloidal suspensions, pressure drop in the CP layer, \( P_p \), is negligible because it is very small compared to the pressure drop in the cake layer. Thus, Eq. (1) simplifies to

\[ \Delta P_c = \Delta P - \Delta P_m = \Delta P - \lambda v_w \]

(12)

Combining Eq. (4), (6), and (12) results in an expression for the cake layer thickness:

\[ \delta_e = \frac{4 \pi a \frac{iD}{3 \theta_{max} kT A_i(\theta_{max})}}{\frac{\Delta P - \lambda v_w}{v_w}} \]

(13)

Assuming that membrane resistance does not change with time, differentiation of Eq. (13) with respect to time yields

\[ \frac{d\delta_e}{dt} = \frac{4 \pi a \frac{iD \Delta P}{3 \theta_{max} kT A_i(\theta_{max})}}{\frac{\Delta P - \lambda v_w}{v_w}} \frac{\Delta P_m}{dt} \]

(14)

Substituting Eq. (14) in Eq. (11) results in

\[ \frac{dv_w}{dt} = \left[ \frac{-3 \theta_{max} kT A_i(\theta_{max}) C_0}{4 \pi a \frac{iD \Delta P}{C_e - C_0}} \right] v_w \]

(15)

Eq. (15) can be converted into a more practical form by integrating it with respect to time:

\[ \frac{v}{v_0} = \left[ 1 + \frac{2 kT A_i(\theta_{max}) C_0 \Delta P}{D \theta(\theta_{max})(C_e - C_0)} t \right]^{1/2} \]

(16)

For dilute colloidal suspensions (i.e., \( C_0 \ll C_e \)), Eq. (16) further simplifies to
\[
\frac{v}{v_0} = [1 + \frac{2kTA(\theta_{\text{eq}})C_s\Delta P}{D_R} t]^{1/2} \tag{17}
\]

Eq. (17) indicates that initial water flux decline rate is a function of hydrodynamic and thermodynamic properties of colloidal suspensions. Rearrangement of Eq. (17) gives the following linear relationship:

\[
[\frac{v}{v_0}]^2 - 1 = Kt \tag{18}
\]

where \( K \) is defined as

\[
K = \frac{2kTA(\theta_{\text{eq}})C_s\Delta P}{D_R} \tag{19}
\]

3. Experimental

3.1 Preparation and Characterization of Colloids

3.1.1 Colloidal Suspensions

Silica (SiO₂) particles (PST1, Nissan Chemical, Tarrytown, NY) were selected as model colloids for the membrane filtration experiments. The particles were received as a 20% (w/w) aqueous suspension with a pH of 10. The manufacturer reports that the particles are spherical having a mean diameter of 0.1 \( \mu \)m and a narrow size distribution. The size and monodispersity of the silica particles were verified by a dynamic light scattering spectrophotometer (Nicomp Model 370, Particle Sizing Systems, Santa Barbara, CA). TEM images were also used to confirm the particle size, monodispersity, and sphericity of the silica colloids. The density of a silica particle measured by gravimetric method was 2.27 g/cm³. This value is very close to that (2.36 g/cm³) calculated based on the reported specific bulk gravity (1.132 at 20°C) of the silica suspension.

3.1.2 Colloidal Stability

The colloidal stability of the silica suspensions was determined by coagulation experiments. In these experiments, 15 ml of pH 10 KCl solutions (10⁻³, 10⁻², 10⁻¹, and 2.5 × 10⁻¹ M) were added to 0.25 ml of 0.02% (v/v) aqueous colloidal silica suspension in 20 ml glass vials. The vials were shaken gently and immediately placed in a dynamic light scattering spectrophotometer for monitoring the particle size evolution with time. The instrument recorded measurements of mean particle diameter every 2 minutes for a total time period of 20 minutes.

3.2 Crossflow Membrane Filtration System

3.2.1 Inorganic Membrane

The membrane selected for the experiments was a ceramic tubular ultrafiltration (UF) membrane (Membralox zirconia membrane, US Filter Corp., Warrendale, PA) with a reported average pore size of 0.02mm. The membrane was 250 mm long and 7 mm in diameter. It was housed in a steel membrane case (US Filter Corp., Warrendale, PA). According to the manufacturer, the membrane can operate at pH range of 0.5 to 13.5 and temperatures from 4 to 316 °C. The permeability of the membrane is reported to be 1.071 × 1.18 × 10⁻⁶ m/s × kPa (15.7 ~ 17.4 gfd/psi) at 20°C.

3.2.2 Crossflow Membrane Filtration Test Unit

The membrane module has one inlet and two outlet ports. The colloidal suspension, held in a 5-liter polypropylene reservoir, is fed to the inlet port of the membrane module by a peristaltic pump (Cole-Parmer Instrument Co., Niles, IL). The flow rate of the feed suspension is measured by a flow meter connected to the inlet of the membrane module. Transmembrane pressure is set by a needle valve installed on the outlet side of the membrane module. The transmembrane pressure is measured by a various reluctance differential pressure.
transducer (Model DP15-44, Validyne Engineering Corp., Northridge, CA) connected to the inlet side of the membrane module. The pressure readings are displayed by a digital transducer indicator (Model CD223, Validyne Corp., Northridge, CA). The transducer can measure pressure drops ranging from 0 to 32 psi with a reported error of ±0.5%. A pressure gauge (Cole-Parmer Instrument Co., Niles, IL) is also used to ensure accurate pressure drop readings. Temperature is controlled by circulating chilled water through a stainless-steel coil immersed in water surrounding the container holding the feed suspension. Chilled water is provided by a refrigerated recirculating chiller (Fisher Scientific, Pittsburgh, PA). One of the module outlet is used to collect the permeate for flux measurements. Permeate flux measurements are done by collecting the permeate in a pre-weighed beaker over a period of 4 or 9 minutes and then weighing the collected permeate to determine the volume collected.

3.3 Crossflow Filtration Experiments
3.3.1 Experimental Procedure
Before each experiment, the membrane was conditioned with a particlefree solution having solution chemistry (described later) identical to that to be used in the subsequent filtration experiment for approximately one hour. Flux measurements for all experiments were taken for a period of 120 minutes, except for the pressure-release experiments (see next section), for which measurements were taken for a total period of 180 minutes. Each permeate sample was collected for a period of 4 minutes during the first 80 minutes of the experiment and for a period of 9 minutes during the last 40 minutes of the experiment.

The filtration system was cleaned before each experiment using a four-step procedure during which transmembrane pressure was kept at zero resulting in no permeate flow through the membrane. The system was first flushed with deionized (DI) water at a high crossflow rate for about 5 minutes. Then, it was cleaned with an acidic HCl solution (pH 3) for 30 minutes followed by a basic wash with NaOH solution (pH 11) for one hour. Both the acidic and basic washes were conducted at moderate crossflow rates. Finally, the system was flushed with DI water again for about 5 minutes.

3.3.2 Experimental Conditions
Filtration experiments were conducted to investigate how variations in primary physical and chemical parameters—particle concentration, transmembrane pressure, shear rate, and ionic strength—would affect permeate flux with time. When varying one of the above conditions, all other remaining conditions were kept constant. The default conditions used included a particle concentration of 0.01% (v/v), a transmembrane pressure of 6 psi (41.4kPa), a crossflow velocity of 0.246 m/s (shear rate of 280 s⁻¹), and an ionic strength of 10⁻² M. All feed suspensions were kept at a pH 10 and at a temperature of 20°C. The pH and ionic strength were adjusted through the addition of NaOH and KCl, respectively.

The varied physical conditions included particle concentrations of 0.005, 0.01, and 0.03% (v/v); transmembrane pressure drops of 3, 6, and 9 psi (20.7, 41.4, and 62.1kPa); and crossflow velocities of 0.246 and 0.492 m/s (shear rates of 280 and 560 s⁻¹). The crossflow velocities of 0.246 and 0.492 m/s correspond to Reynolds numbers of 1700 and 3400, respectively (Reynolds number was calculated on the basis of crossflow veloci-
ty and membrane cylindrical channel diameter). In addition, the effect of ionic strength on transient permeate flux was studied by varying KCl concentration (10⁻³, 10⁻², and 10⁻¹ M).

3.3.3 Pressure-Release Experiments
Pressure-release experiments were conducted to investigate the reversibility of the cake layer at three different ionic strengths (10⁻³, 10⁻², and 10⁻¹ M KCl). Following the 3 hours of membrane filtration experiment, the transmembrane pressure was reduced to zero by opening the needle valve while maintaining all other experimental conditions constant. After the 1 hour of pressure-release, the valve was partially closed again to obtain the same transmembrane pressure of 6 psi (41.4 kPa) as in the first membrane filtration experiment. Flux measurements were then taken for a period of 60 minutes.

3.3.4 Determination of Cake Layer Porosity
Experiments were also conducted to determine possible variation of cake porosity with time during the crossflow filtration. In these experiments, the mass of the deposited cake layer was determined by collecting samples of the feed at predetermined time intervals during the 120-minute long filtration experiments. A feed sample was collected at the start of the experiment and every 20 minutes for the ensuing 120 minutes of the experiments. The samples were collected using a 20 ml volumetric pipette. The samples were then analyzed for particle concentration by a UV/VIS spectrophotometer (Model 8452A, Hewlett Packard, Palo Alto, CA). By subtracting the amount of particles left in the feed suspension after each collection period from the initial amount of particles in the suspension, the cumulative amount of deposited particles on the membrane surface was readily obtained.

4. Results and Discussion

4.1 Colloidal Suspensions and Inorganic Membrane
4.1.1 Silica Colloids
The kinetic model developed in this study involves a monodispersed, spherical, and non-interacting colloidal suspension. Particle size, shape, and monodispersity are critical in evaluating the dynamic behavior of permeate flux decline because these factors markedly affect the hydraulic resistance of the particle cake layer [Tarleton, and Wakeman, 1993; Lojkine et al., 1992]. The silica particle suspension selected for our study meets these model requirements. Particle size measurements by dynamic light scattering show that silica particles have a mean diameter of 0.11 μm with a narrow size distribution. TEM images verified the monodispersity and sphericity of the silica suspension.

Colloidal stability experiments demonstrate that the silica suspension is quite stable at the ionic strengths employed in the filtration experiments (i.e. Fig. 1. Particle Size Evolution with Time at Different Ionic Strengths (2.5 × 10⁻¹, 10⁻², 10⁻³ M). Lonic Strength is Adjusted by Varying KCl Concentration. Particle Size is Measured by Dynamic Light Scattering (DLS).
membrane tested in our study exhibited a specific membrane permeability in the range of $0.72 \sim 0.82 \times 10^{-4}$ m/s×kPa, depending on chemical and hydrodynamic conditions. This value is slightly smaller than that reported by the manufacturer ($1.07 \sim 1.18 \times 10^{-6}$ m/s×kPa). One hour of stabilization was adequate to achieve a steady-state flux. Rejection of small solutes, such as KCl, by the membrane was nearly zero, implying no elevated solute concentration at the membrane surface. Silica particles, on the other hand, were completely retained by the zirconia membrane.

4.2 Model Application

The kinetic model suggests that physical parameters, such as particle concentration and transmembrane pressure, have a marked influence on the dynamic behavior of permeate flux decline. In this study, a series of crossflow membrane filtration experiments were performed to investigate systematically the effect of these parameters on transient permeate flux. Experimental results were compared with theoretical values predicted by the model.

4.2.1 Effect of Particle Concentration

Fig. 2 illustrates the effect of particle concentration on permeate flux decline. Each of the filtration experiments was repeated more than twice and the results were very reproducible. According to Fig. 2, the rate of permeate flux decline increases with increasing particle concentration. Experimental results are in a fairly good agreement with theoretical predictions. This phenomenon is attributed to an increase in particle transfer rate to the cake layer at high particle concentration. According to the simplified mass balance equation, Eq. (11), the growth of the cake layer is proportional to particle flux ($v_w \times C_0$) entering
the cake layer. Thus, an increase in particle bulk concentration enhances particle accumulation in the cake layer, resulting in increased hydraulic resistance of the cake layer.

Similar trends have been observed in numerous studies. Tarleton and Wakeorman [1994] showed that permeate flux declines much faster with increasing particle concentration. Theoretical and experimental studies by Romero and Davis [1989; 1991] also reported similar observation. In addition to increased particle deposition, there has been experimental evidence showing the formation of a more closely packed cake layer at high particle concentration. Chudacek and Fane [1984] demonstrated that the specific resistance of the silica cake layer, calculated from Kozeny-Carman equation, increases with increasing particle concentration. This may be the result of the increased pressure that accumulated particles at the top of the cake layer exert on the particle in the bottom of the layer.

4.2.2 Effect of Transmembrane Pressure

The effect of transmembrane pressure on transient permeate flux is presented in Fig. 3.

Results show that permeate flux declines more rapidly with increasing transmembrane pressure. This observation can be attributed to two factors: the thickness of the cake layer and the compactness of the cake layer. Particle accumulation in the cake layer is enhanced as transmembrane pressure increases because particle flux into the cake layer increases due to increased permeate flux. Furthermore, the cake layer is more compressed at high transmembrane pressure due to the drag force induced by permeate flow. As a result, the hydraulic resistance of the cake layer becomes larger and the permeate flux is substantially reduced. Under given chemical and physical conditions, experimental results show a relatively good agreement with theoretical predictions.
The importance of transmembrane pressure (i.e. initial permeate flux) in membrane filtration of colloidal suspensions has been experimentally demonstrated by various researchers. Romero and Davis [1991] showed faster decline of permeate flux with increasing initial permeate flux. Similar observation was reported by Tarleton and Wakeman [1994]. It has also been shown that the cake layer becomes more densely packed as transmembrane pressure increases [Chudacek and Fane, 1984]. The extent of cake compressibility, however, is largely dependent on solution chemistry of the feed suspension, indicating that the porosity of the cake layer is a function of both physical (i.e. hydrodynamic) and chemical (i.e. colloidal) interactions. This will be discussed in detail in the following section.

4.3 Role of Colloidal Interactions

As mentioned previously, colloidal interactions play a significant role in membrane filtration of submicron colloidal suspensions. In this section, the effect of colloidal interactions on transient permeate flux is investigated at various permeate velocities and crossflow velocities. Colloidal (i.e. double layer) interaction is adjusted by varying solution ionic strength (KCl concentration).

4.3.1 Effect of Ionic Strength

In order to investigate the influence of colloidal interactions, filtration experiments were conducted at three different concentrations of an indifferent salt (10^{-3}, 10^{-2}, and 10^{-1}M KCl). Fig. 4 demonstrates that the decline of permeate flux becomes more severe as ionic strength of the feed suspension increases.

This phenomenon can be explained by an increase in the hydraulic resistance of the particle deposit layer at high ionic strength. Increased hydraulic resistance may be attributed to enhanced deposition of colloidal particles onto the membrane surface and dense structure of the colloidal cake layer. Enhancement of colloidal deposition is ascribed to the decrease in double layer repulsion between the negatively-charged membrane and the silica particles as the ionic strength increases. (Note that the isoelectric points of zirconia and silica are approximately 4 ~ 5 and 2 ~ 3, respectively, and the pH of the feed suspension is maintained at 10.) A recent theoretical study by Song and Elimelech [1995a] showed that particle deposition rate increases with increasing solution ionic strength. In our study, deposited mass of silica particles was measured from depletion of feed particle concentration to verify the effect of colloidal interactions on colloidal deposition. Results are presented in Fig. 5.

Unlike theoretical predictions, solution ionic strength has only a minor influence on colloidal deposition, although a small increase in deposit mass is ob-
served with increasing ionic strength. This observation suggests that the increase in hydraulic resistance at high ionic strength is rather related to the packing of the cake layer as will be shown later in this section.

The lack of particle deposition discussed above can be explained by the colloidal stability of the silica suspension. Colloidal stability experiments (Fig. 1) showed that the silica suspension is very stable at the ionic strengths investigated, suggesting that silica deposition onto zirconia membrane or previously deposited silica particles is independent of ionic strength (up to $10^{-1}$ M). Thus, silica particles are held in the cake layer physically by permeate flow, not by chemical particle–membrane or particle–particle interactions. This conclusion is further verified by studying the reversibility of the cake layer as discussed in the following section.

Solution ionic strength also affects the structure of the cake layer [Bacchin et al., 1996; McDonogh et al., 1984; 1989]. Recently, several theoretical studies have attempted to determine permeate flux based on a force balance in the particle deposit layer [Welsch et al., 1995; McDonogh et al., 1992]. In these studies, interparticle spacing (i.e. porosity of the particle deposit layer) is calculated by balancing forces (e.g. permeation drag, double layer repulsion, and van der Waals attraction) acting on the particle [Bowen and Jenner, 1995b; Petsev et al., 1993]. Permeability of the particle deposit layer is then estimated from the calculated porosity using either Happel or Kozeny–Carmen equation [Bowen et al., 1996; Bowen and Williams, 1996; Jonsson and Jonsson, 1996; Petsev et al., 1993]. In our study, transient variations in cake porosity at three different ionic strengths are calculated by fitting permeate fluxes based on the experimentally measured particle deposit mass shown in Fig. 5. Results are presented in Fig. 6.
At the given hydrodynamic conditions, the porosity of the cake layer decreases with increasing ionic strength. It is also observed that the porosity of the cake layer decreases with time. In our kinetic model, the porosity of the cake layer is assumed to be a constant value, 0.36 (v/v), based on a random packing density. However, it is clearly shown that the porosity of the cake layer changes with solution chemistry. In addition, the cake layer is consolidated as time progresses.

4.3.2 Effect of Permeate Velocity

As mentioned previously, both particle deposition on the membrane surface and particle concentration in the cake layer are determined by the combined effect of various physical and chemical interactions. Song and Elimelech [1995b] demonstrated that particle deposition rate on the membrane surface is mainly influenced by an interplay between permeation drag and double layer repulsion. They also showed that particle deposition increases sharply at a permeate flux above which permeation drag dominates double layer repulsion. This so called critical flux, defined as the permeate flux below which a decline in permeate flux does not occur, has been experimentally observed by numerous researchers [Howell, 1995; Field et al., 1995; Cohen and Probstein, 1986]. In addition, it has been theoretically and experimentally demonstrated that the porosity of the particle deposit layer is mainly determined by a balance between permeation drag force and double layer repulsion [Bowen and Jenner, 1995b; Petsev et al., 1993; McDonogh et al., 1984]. In our study, the effect of permeate velocity on transient flux is systematically studied at three different ionic strengths. Results are analyzed based on Eq. (18) (Fig. 7).

The graph (i.e. K) increases as permeate velocity increases. It is also observed that, at a constant permeate flux, the slope of the graph increases with increasing solution ionic strength. However, the existence of a critical flux (i.e. K = 0), even though strong double layer repulsion is anticipated at low ionic strength (10^-3 M KCl) and low permeate flux (3 psi transmembrane pressure), is not observed in this investigation.

4.3.3 Effect of Crossflow Velocity

Fig. 8 represents the effect of crossflow velocity (shear) on transient flux at three different ionic strengths. Regardless of ionic strength, the rate of permeate flux decline at low crossflow velocity (0.246 m/s or 280 s^-1 shear) is almost identical to that at high crossflow velocity (0.492 m/s or 560 s^-1 shear), suggesting that the crossflow velocity has a negligible influence on transient flux. Numerous studies have demonstrated that crossflow velocity has a significant
influence on permeate flux decline. Generally, permeate flux declines much slower at high crossflow velocity because of various transport mechanisms induced by shear. However, enhancement of permeate flux due to shear is only applicable to large particles (i.e. \( a_p > 1 \mu m \)) and less pronounced as particle size decreases. For submicron colloidal particles, crossflow velocity has only a small effect on permeate flux. Cohen and Probsttein [1986] have shown that, under laminar flow condition, the growth of the colloidal cake layer is a weak function of shear. Romero and Davis [1990] have also indicated that transient flux decline is independent of the crossflow until a steady-state flux is established, implying that a dead-end filtration theory may be adequate to predict an initial water flux decline.

4.4 Reversibility of the Cake Layer
In order to examine the reversibility of cake formation, pressure release experiments were conducted at three different ionic strengths \( (10^{-4}, 10^{-2}, \text{and} \ 10^{-3} \text{M KCl}) \) [Benkahla et al., 1995]. Dynamic behaviors of permeate flux decline before and after transmembrane pressure is released are compared in Fig. 9.

It is clearly shown that, regardless of ionic strength, permeate flux is completely recovered after 1 hour of pressure-relaxation. This finding suggests that cake formation is reversible and membrane fouling (i.e. irreversible adsorption within membrane pore or onto membrane surface) does not occur at the chemical and physical conditions investigated. As soon as transmembrane pressure is reduced to zero, silica particles diffuse away from the membrane surface because of concentration gradient. Since there is no particles irreversibly deposited within membrane pores or onto membrane surface, all of silica colloids

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Fig. 8. Effect of Crossflow Velocity (shear \( 280 \) and \( 560 \text{ s}^{-1} \)) on Transient Permeate flux at Three Different Ionic Strengths \( (10^{-4}, 10^{-2}, \text{and} \ 10^{-3} \text{M KCl}) \). Experimental Conditions: Transmembrane Pressure = 6 psi \((41.4 \text{ kPa})\), Temperature = 20°C, pH = 10, and Particle Concentration = 0.01% v/v.

Fig. 9. Permeate Flux Decline with Time Before and After Pressure Release at Three Different Ionic Strengths \( (10^{-4}, 10^{-2}, \text{and} \ 10^{-3} \text{M KCl}) \). Transmembrane Pressure is Adjusted to Zero After 180 minutes of Filtration. After 1 hour of Pressure Release, Transmembrane Pressure is Adjusted back to 6 psi. Experimental Conditions: Transmembrane Pressure = 6 psi \((41.4 \text{ kPa})\), Shear rate = \( 280 \text{ s}^{-1} \), Temperature = 20°C, pH = 10, and Particle Concentration = 0.01% v/v.
accumulated in the cake layer are removed from the membrane surface and, as a result, permeate flux is completely recovered.

In addition to complete flux recovery, it is observed that the rate of permeate flux decline after pressure-release is almost identical to that of the initial membrane filtration. This result implies that there is no coagulation of silica colloids in the cake layer. As discussed previously, silica particles are held in the cake layer by the combined effect of hydrodynamic force (i.e. permeate drag) and colloidal interactions (i.e. double layer repulsion). Due to the high stability of the silica suspension, silica colloids do not coagulate in the cake layer. As a result, they diffuse away from the membrane surface with no change in size after pressure is released.

5. Conclusions

Physical and chemical aspects of transient permeate flux decline in crossflow membrane filtration of colloidal suspensions have been systematically studied. Results are compared with theoretical predictions by a transient permeate flux model developed based on hydrodynamics and thermodynamics of colloidal suspensions. Experimental results demonstrate that permeate flux declines much faster with increasing particle concentration and transmembrane pressure, implying particle convection-controlled permeate flux decline. Under the given chemical conditions (10^{-2} M KCl, pH 10), experimental results show a fairly good agreement with theoretical predictions. Experimental observations also indicate that colloidal interactions have a significant influence on permeate flux decline. Permeate flux decline rate increases as the ionic strength of the feed suspension increases. This phenomenon is attributed to the formation of a more densely-packed cake layer resulting from reduced electrostatic repulsion among the accumulated particles. Under laminar flow conditions, crossflow velocity (shear) has a very small effect on permeate flux, indicating that the approximate kinetic model developed may be adequate to describe the initial flux decline during crossflow membrane filtration of colloidal suspensions. Finally, it is shown that the formation of particle cake layer is reversible, implying no irreversible adsorption of particles to the membrane surface at given chemical and physical conditions.

References


