Blocking Resistance of Membrane during Cake Filtration of Dilute Suspensions

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Clarification of very dilute suspensions of fine particles using microfiltration membranes is being increasingly applied in such water-purification processes as ultrapure water production, sterile water production, effluent polishing, and radioactive contaminants processing.[1] One of the critical issues in the development of effective processes is a rapid flux decline attributed to pore-blocking phenomena arising from particles reaching the membrane as well as the formation of the filter cake.[2] It is thus important to be able to accurately evaluate the dynamic behaviors of both pore plugging and cake formation to facilitate the design of process and operation conditions.

Most previous studies of medium clogging during cake filtration have pertained to either the blocking filtration theory or the deep-bed filtration theory.[3-8] Tiller et al.[9] empirically derived the correlation on the clogged medium resistance R_m, changing with time, to examine clogging phenomena in cake filtration of liquefied coal, as follows

$$\frac{R_m - R_{m0}}{R_{m\infty} - R_{m0}} = 1 - \exp(-\eta w) \tag{1}$$

where R_{m0} and $R_{m\infty}$ are the medium resistance at the initial time and infinite time limit, respectively; w is the net mass of particles within the filter cake per unit effective medium area; and η is the empirical constant. Matsumoto et al.[5] proposed the filtration model in which the particles permeate through the formed filter cake on the basis of the mechanism of deep-bed filtration and some of pores of the medium still remain open eventually. Similarly, Tien et al.[7] analyzed the fine particle retention effect in filter cakes as a deep-bed filtration problem, taking the internal structure of filter cakes into account. Recently, Lee[8] clarified the theoretical background of Eq. 1, and evidenced the physical implication for the parameter η. Moreover, he proposed the newly developed, more rigorous equation to interpret the experimental data of medium clogging on the basis of the intermediate blocking law for clarification filtration with relatively thin medium. The proposed equation has two fitting parameters, η and λ, as follows

$$\frac{R_m - R_{m0}}{R_{m\infty} - R_{m0}} = \frac{1 - \exp(-\eta w)}{1 + \lambda \exp(-\eta w)} \tag{2}$$

In the present article, a simple and reasonable filtration model is developed of the dynamic behaviors of microfiltration in which the pore blocking occurs during cake filtration. The validity of the model is supported by the measured data for microfiltration of very dilute suspensions of fine particles through track-etched membranes performed under various conditions.

Development of Filtration Model

To quantify the filtration behaviors in which the blocking of membrane pores and the filter cake formation brought about by the convective transport of particles toward the membrane surface occur simultaneously and continuously, it is necessary that the filtration resistances induced by these fouling phenomena are evaluated individually. The clogged membrane and filter cake may be considered as two resistances in series by the resistance-in-series model based on the cake filtration theory, and the filtration rate q is then related to the total filtration resistance R_t, the clogged membrane resistance R_m, and the filter cake resistance R_c as

$$q\left(\equiv \frac{dv}{d\theta}\right) = \frac{p}{\mu R_t} = \frac{p}{\mu(R_m + R_c)} \tag{3}$$

where v is the cumulative filtrate volume collected per unit effective membrane area, θ is the filtration time, p is the applied

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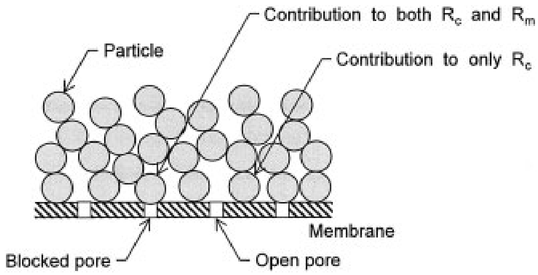

Figure 1. Pore blocking and filter cake formation.

filtration pressure, and μ is the viscosity of the filtrate. The system considered is for a situation where all the particles retained by the membrane contribute the cake resistance R_c and a part of them also serve as the clogged membrane resistance R_m by clogging the membrane pores, as illustrated in Figure 1.

Assuming the filtration rate q is directly proportional to the number of open pores, q can be also written using the total (initial) number n_0 of pores and the number n of clogged pores, as

$$q = k(n_0 - n)p_m = \frac{p_m}{\mu R_m} \tag{4}$$

where p_m is the pressure loss across the clogged membrane, equivalent to the difference between the total pressure loss p and that across the filter cake, and k is the constant defined by Eq. 4. The clogged membrane resistance R_m is therefore related to either q or n by Eq. 4. On the basis of Eq. 4, the number ($n_0 - n$) of open pores at an arbitrary time is represented by

$$n_0 - n = \frac{1}{\mu k R_m} \tag{5}$$

Similarly, the initial number n_0 of open pores is given by

$$n_0 = \frac{1}{\mu k R_{m0}} \tag{6}$$

Assuming that the number of clogged pores finally reaches the limited value n_1 ($n_1 < n_0$) and as a consequence ($n_0 - n_1$) pores remain open, the final number ($n_0 - n_1$) of open pores is expressed as

$$n_0 - n_1 = \frac{1}{\mu k R_{m\infty}} \tag{7}$$

One of the implications of the model is that the final membrane resistance $R_{m\infty}$ is not infinity but a finite value as shown in Eq. 7, and thus the filtration flux never becomes zero at the end of the pore-blocking process. Therefore, our model is realistic and reasonable.

The pore-blocking behavior is essentially governed by the stochastic phenomena. By considering the stochastic process in the intermediate blocking law that the probability of the membrane clogged at an arbitrary time is proportional to the number ($n_0 - n$) of open pores, the variation of the number n of clogged pores is expressed as

$$n = n_1\{1 - \exp(-\eta w)\} \tag{8}$$

By substituting Eqs. 5–7 into Eq. 8, one obtains the final expression for describing the clogged membrane resistance R_m as

$$\frac{1 - R_{m0}/R_m}{1 - R_{m0}/R_{m\infty}} = 1 - \exp(-\eta w) \tag{9}$$

Equation 9 is attractive because of its simplicity, given that the relation between R_m and w can be determined by only one adjustable parameter η. This is an advantage of our model.

Experimental

An unstirred batch filtration cell (KS-25, Advantec Toyo Corp.) with an effective membrane area of 3.33 cm^2 was used in this research. The track-etched polycarbonate membranes with nominal pore sizes d_m of 0.05, 0.1, 0.2, 0.4, and 0.6 μm, supplied by Nuclepore Corp., were used for all experiments. The membranes have extremely sharp size distribution of the cylindrical pores. Dead-end microfiltration experiments were performed under various constant pressure conditions ranging from 98 to 294 kPa controlled by a reducing valve by applying compressed nitrogen gas after the dilute suspensions were poured into both the filtration cell and the feed reservoir connected to the cell. The weight of the filtrate produced during the course of filtration was measured with an electronic balance connected to a personal computer to collect and record mass vs. time data. The weights were converted to volumes using density correlations. The filtration rate was obtained by numerical differentiation of the volume vs. time data. In addition, the variations of the particle concentration in the filtrate with time were indirectly measured by reading the absorbance at a wavelength of 306 nm to investigate the rejection of particles by the membrane.

The particles used in the experiments were monodisperse polystyrene latex (PSL) with particle diameters of 0.522 and 0.091 μm (Dow Chemical Japan Ltd.) and multidisperse fine silica colloids (SiO_2) with a mean diameter of 1.33 μm (Kojundo Chemical Laboratory Co., Ltd.). The particles were suspended in ultrapure, deionized water obtained by filtering distilled water through a Milli-Q SP water system (Millipore Corp.). The particle concentration s by weight ranged from 1 to 5×10^{-6} for polystyrene latex and was 1×10^{-5} for fine silica colloids.

Results and Discussion

In Figure 2, the typical flux decline data for dead-end microfiltration, using very dilute polystyrene latex suspensions at various particle concentrations and applied pressures, are plotted in the form of the reciprocal filtration rate ($d\theta/dv$) vs. the cumulative filtrate volume v per unit effective membrane area, which is well known as the Ruth plot,[10] classically used in the ordinary cake filtration. The cake filtration model implies that the plot of $d\theta/dv$ against v for constant pressure process be-

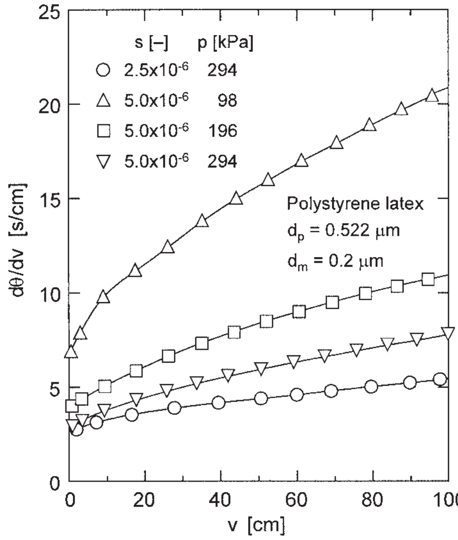

Figure 2. Plots of reciprocal filtration rate as a function of filtrate volume per unit membrane area for microfiltration of very dilute polystyrene latex suspensions.

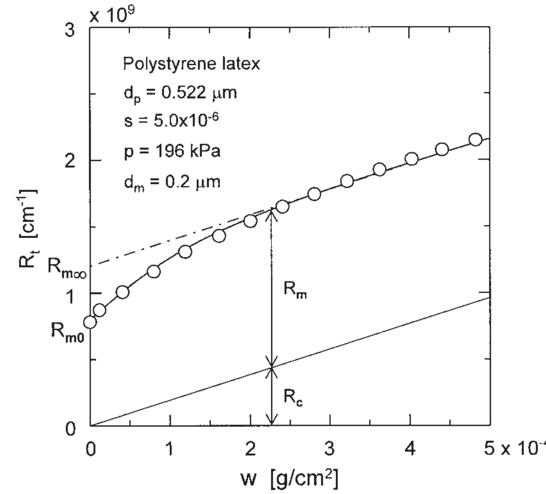

Figure 3. Dynamic behavior of resistances of blocked membrane and filter cake observed from relation between total filtration resistance and net mass of particles within filter cake per unit membrane area.

comes substantially linear over the course of filtration in accordance with the Ruth filtration rate equation[10] resulting from the continuous growth of a filter cake on the membrane when the fouled membrane resistance is negligible compared with the filter cake resistance. The plots in the figure for any condition, however, are nonlinear (convex upward) at small v-values. As expected, this means the effect of the pore blocking is more pronounced.

On the basis of the filtrate flux data presented in Figure 2, the relation between the total filtration resistance R_t calculated from Eq. 3 and the dry cake mass w per unit membrane area can be obtained. On the assumption that all the particles deposited on the membrane act as the filter cake that generates the hydraulic resistance R_c and a part of them that approach the pores of the membrane contribute to an increase of the clogged membrane resistance R_m by sealing the membrane pores, a contribution of R_c and R_m to the total filtration resistance R_t can be illustrated as in Figure 3. Because the polystyrene particles with a diameter d_p of 0.522 μm are rejected almost completely by 0.2-μm pore size membrane, w can be obtained using the relation, $w = \rho s v$, where ρ is the density of the filtrate. The value of R_c increases with w as a result of cake formation on the membrane surface, and the relation can be represented by a straight line through the origin with a slope of the latter linear part of the R_t profile against w. The average specific filtration resistance α_{av} of the filter cake is obtained from the slope, using the relation $R_c = \alpha_{av} w$. The clogged membrane resistance R_m can be obtained by subtracting R_c from R_t. The figure shows that the initial membrane resistance R_{m0} corresponds to R_t at $w = 0$, whereas the final membrane resistance $R_{m\infty}$ corresponds to the intercept obtained by extrapolating the latter linear part of the R_t profile against w. Initially, R_m is equivalent to R_{m0}, and increases with filtration time approaching $R_{m\infty}$.

In Figure 4, the variations of R_m with time in microfiltration of polystyrene latex suspensions performed using 0.2- and 0.6-μm pore size membrane under various experimental conditions are plotted in the form of the left-hand side of Eq. 9 obtained using R_{m0} and $R_{m\infty}$ against the dry cake mass w. These data are compared with the calculations based on Eq. 9 using the fitting parameter η determined to fit experimental data. For the 0.6-μm pore size membrane, an influence of a small leakage of 0.522-μm particles passing through the membrane with the filtrate in the initial stage of filtration was accounted for in the calculation of the experimental values of w from the filtrate volume v. The figure clearly demonstrates that the experimental data can be satisfactorily described by the model calculations. The fitting parameter η, which is a measure of the progress rate of the pore blockage, for 0.6-μm pore size membrane ($\eta = 1.2 \times 10^5$ cm^2/g) is much larger than that for 0.2-μm pore size membrane ($\eta = 1.2 \times 10^4$ cm^2/g). It can also be seen that the value of η is largely unaffected by the bulk

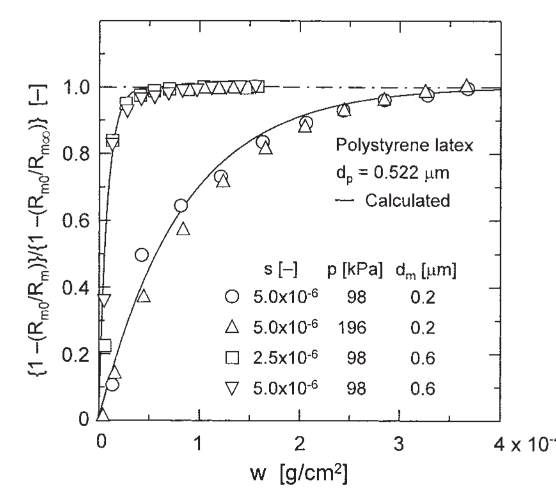

Figure 4. Plots of lefthand side of Eq. 9 as a function of net mass of particles within filter cake per unit membrane area for microfiltration of very dilute polystyrene latex suspensions.

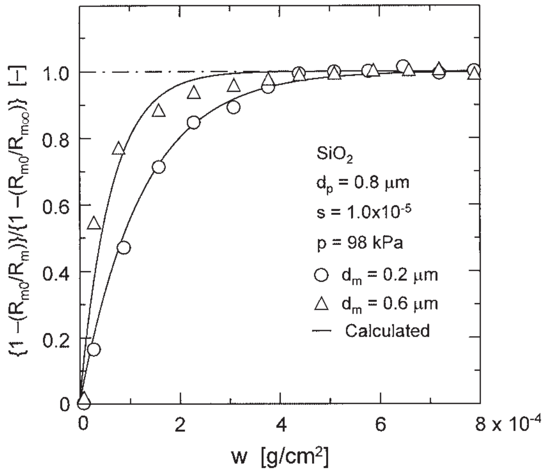

Figure 5. Plots of lefthand side of Eq. 9 as a function of net mass of particle within filter cake per unit membrane area for microfiltration of very dilute fine silica colloids.

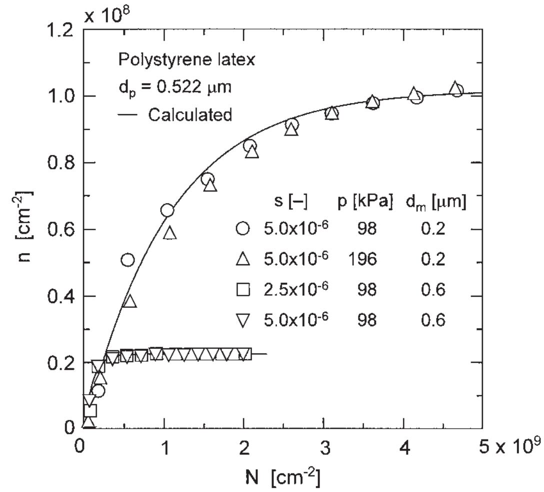

Figure 6. Relation between number of blocked pores and number of deposited particles for microfiltration of very dilute polystyrene latex suspensions.

particle concentration and the applied pressure when the same pore size membranes are used. Likewise, shown in Figure 5 are the experimental data for fine silica colloids along with model calculations. The calculations are fairly consistent with the experimental data, which suggests that the model is applicable to not only monodisperse systems but also multidisperse systems. The fitting parameter η for 0.6-μm pore size membrane ($\eta = 1.6 \times 10^4$ cm^2/g) is larger than that for 0.2-μm pore size membrane ($\eta = 8.0 \times 10^3$ cm^2/g), similar to the results seen in Figure 4. Almost the same predictions as those shown in Figures 4 and 5 can be obtained using the appropriate values of η and λ on the basis of Eq. 2 proposed by Lee.[8] However, only one fitting parameter is involved in Eq. 9, whereas the calculations based on Eq. 2 require two fitting parameters.

The data in Figure 4 are converted into the form of the number n of blocked pores existing on the unit membrane area vs. the number N of particles deposited as a cake per unit membrane area, and they are shown in Figure 6. The number n can be determined by using the number density of the pores of the membrane used, and the number N can be obtained by dividing the dry cake mass w by the mass of a particle. The number of blocked pores is increased and approaches a plateau with increasing number of deposited particles. The pore blocking of 0.2-μm pore size membrane tends to approach a plateau more slowly compared with that of 0.6-μm pore size membrane. It is emphasized, however, that the final number of blocked pores of 0.2-μm pore size membrane is much larger than that of 0.6-μm pore size membrane.

On the basis of Eqs. 6 and 7, the final pore-blocking ratio B_∞, defined as the fraction of the final number n_1 of blocked pores of the membrane to the total number n_0 of pores, can be represented as

$$B_\infty\left(\equiv \frac{n_1}{n_0}\right) = 1 - \frac{R_{m0}}{R_{m\infty}} \tag{10}$$

In Figure 7, B_∞ is plotted as a function of the ratio r of the pore size d_m to the mean particle size d_p. It is important to note that the final pore-blocking ratio B_∞ tends to increase with increasing size ratio r. This trend of plots in the figure is plausible because it is appropriate that the value of B_∞ should be zero when the pore size is zero. The most striking feature is that the data at various conditions clearly collapse to a single curve when plotted in this fashion. It is significant that the final state of the pore blocking can be evaluated by using this relation if the size ratio r is given.

It is essential for the understanding of pore-blocking behaviors to clarify the major factor influencing the rate at which the pore blocking proceeds. In Figure 8, the coefficient η, which is a measure of the pore-blocking rate, is plotted against the final number n_1 of blocked pores. The blocking rate was found to be intimately linked to the number n_1 of the blocked pores and to decrease monotonically with increasing n_1. It was also found that the blocking rate in microfiltration of fine silica colloids is much lower than that in the polystyrene latex.

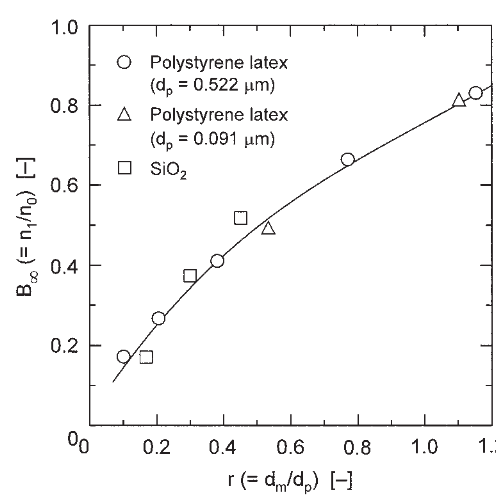

Figure 7. Relation between final pore-blocking ratio and ratio of pore size to mean particle size.

In Figure 9, the variations of the reciprocal filtration rate ($d\theta/dv$) with the filtrate volume v observed in microfiltration experiments of very dilute polystyrene latex and fine silica colloids are compared with the calculations based on our model for various conditions of the bulk particle concentration and the pore size of the membrane. The calculations were obtained by combining Eq. 3 with Eq. 9, using the relations, $R_c = \alpha_{av}w$ and $w = \rho sv$. The values of R_{m0}, $R_{m\infty}$, and α_{av} were determined to fit the experimental data, as shown typically in Figure 3. Finally, the value of η was determined as the fitting parameter. The model predictions agree closely with the measured values for various conditions, supporting the validity of the model.

Conclusions

The simple and convenient filtration model in which only one fitting parameter is involved has been developed to describe the blocking phenomenon of the membrane pores. The validity of the model described was examined experimentally by conducting microfiltration of very dilute suspensions of monodisperse polystyrene latex and multidisperse fine silica colloids using the track-etched polycarbonate membrane. The predicted and measured results were in fair agreement for a variety of conditions, such as the filtration pressure, the bulk particle concentration, and the pore size of the membrane. Thus, it was concluded that the proposed model was capable of representing the complex filtration process where the pore blocking and the cake formation occurred simultaneously. Moreover, the factors influencing the properties of the pore blocking, such as the coefficient η associated with the blocking rate and the final pore-blocking ratio B_∞, were revealed.

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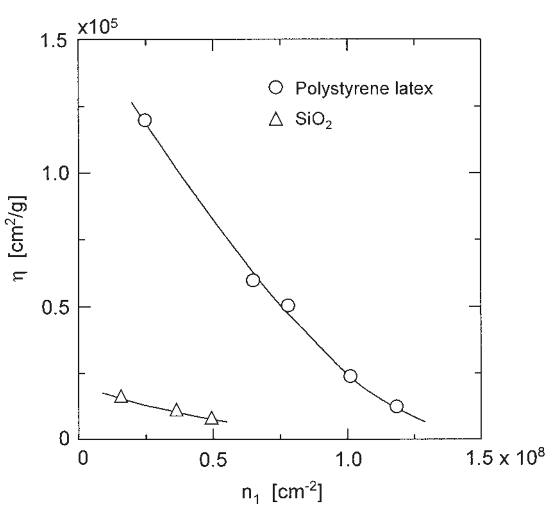

Figure 8. Relation between coefficient η and final number of blocked pore.

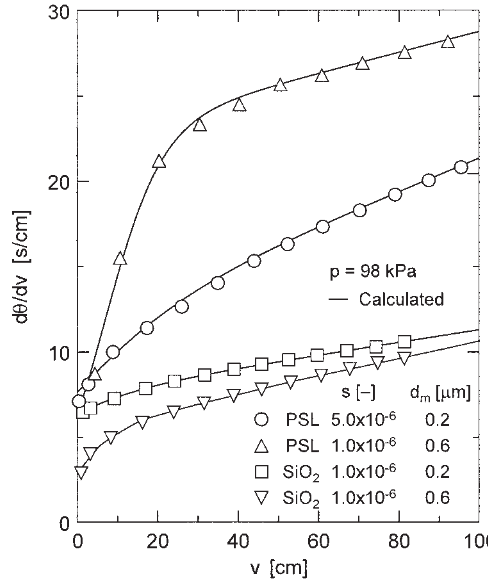

Figure 9. Comparison of reciprocal filtration rates predicted by model with those obtained from microfiltration of very dilute particulate suspensions under various conditions.

Notation

B_∞ = final pore-blocking ratio
d_m = pore diameter, m
d_p = mean particle diameter, m
k = coefficient defined by Eq. 4, $m^4\ s\ kg^{-1}$
N = number of particle deposited per unit effective membrane area, m^{-2}
n = number of blocked pore per unit effective membrane area, m^{-2}
n_0 = total number of pore per unit effective membrane area, m^{-2}
n_1 = final number of blocked pore per unit effective membrane area, m^{-2}
p = applied filtration pressure, Pa
p_m = pressure loss across membrane, Pa
q = filtration rate, m/s
r = ratio of pore diameter to mean particle diameter
R_c = filter cake resistance, m^{-1}
R_m = membrane resistance, m^{-1}
R_{m0} = initial membrane resistance, m^{-1}
$R_{m\infty}$ = final membrane resistance, m^{-1}
R_t = total filtration resistance, m^{-1}
s = mass fraction of particle in suspension
v = cumulative filtrate volume per unit effective membrane area, m^3/m^2
w = net mass of particle within filter cake per unit effective membrane area, kg/m^2

Greek letters

α_{av} = average specific filtration resistance of filter cake, m/kg
η = coefficient defined by Eq. 8, m^2/kg
θ = filtration time, s
λ = empirical constant in Eq. 2
μ = viscosity of filtrate, Pa·s
ρ = density of filtrate, kg/m^3

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