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The Role of Dynamic Membrane in Cross-Flow Microfiltration of Macromolecules

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ABSTRACT

The effects of dynamic membrane formed by fine particles on the filtration rate and the rejection of macromolecules in cross-flow microfiltration are studied. Experiments were carried out using the binary suspensions prepared by polymethyl methacrylate (PMMA) particles and the Dextran macromolecules. The filtration rates, the rejections of Dextran and the cake properties under various operating conditions, such as the cross-flow velocity and the filtration pressure, are measured and discussed. The filtration rate increases with increases of the cross-flow velocity and the filtration pressure but decreases when the molecular weight of Dextran is increased. On the other hand, the rejection of Dextran increases with the increase of filtration pressure but decreases with the increase of cross-flow velocity. The standard capture equation for deep-bed filtration is adopted to relate the rejection of Dextran and the properties of dynamic membrane. The results show that the mass of

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the dynamic membrane is the most important factor on the rejection of Dextran. Using the experimental data obtained under various cross-flow velocities, the rejection of Dextran can be regressed as a single function of cake mass. It can be concluded that the rejection of macromolecules increases due to the presence of fine particles, and that the magnitude of the rejection increases with increasing the mass of cake.

Key Words: Cross-flow microfiltration; Dynamic membrane; Rejection of macromolecules; Membrane separation.

INTRODUCTION

Cross-flow microfiltration is an economic and efficient method for solid–liquid separation of fine particles, colloids, or macromolecules. This unit operation has been widely used in various fine chemical or biochemical processes; however, the mechanism of this mode of filtration has not been well understood, especially when fine particles and macromolecules are coexistent in the suspensions.

Various models or theories have been proposed to relate the filtration rates to the operating conditions in cross-flow microfiltration. According to the concentration polarization models,[1] the rejected solute particles formed a concentration polarization layer near the membrane surface. Based on this model, the convective flux of particles toward the membrane was balanced by the diffusion flux away from the membrane at the steady state. The steady filtration rate then could be estimated in accordance with the "film theory" once the values of particle diffusivity and the concentration at the membrane surface were known.[1] On the other hand, the hydrodynamic models analyzed the flow field of fluid and the trajectories of particles in the cross-flow filtration systems.[2,3] The concentration profile in the filter and the transported flux of particles arriving at the membrane surface could be calculated using the equation of mass transfer. However, the treated suspensions in most of the previous researches in this field contained only a single component.

The solid–liquid separations of binary suspensions often occur in biochemical or food processes. It is a very important course in these fields to understand how to improve the purification efficiency of macromolecules or colloids, such as proteins or polysaccharides. In recent years, many researchers have kept their focuses on the performances of

microfiltration or ultrafiltration of binary protein systems. The filtration rate and the rejection of proteins are two major factors to characterize a filtration process. In the study of Matsuyama et al.,[4] the dynamic membranes were formed in ultrafiltration of a mixture of ovalbumin and γ-globulin proteins. They concluded that the formation of deposits occurred independently for the two proteins, and that the flux at steady state in the binary protein system agreed with the smaller flux in the corresponding single protein system. Dead-end ultrafiltration of the mixtures of bovine serum albumin (BSA) and egg white lysozyme were conducted in the research of Iritani et al.[5] The used membranes allowed the lysozyme to permeate through but retained BSA completely. The effects of pH and salt concentration in the suspensions on the filtration rate and the lysozyme rejection were discussed. A strong dependence of the filtration rate and the protein rejection on the electrostatic interactions between proteins was found. Arora and Davis[6] used the yeast cake layers as secondary membranes in dead-end microfiltration of BSA to reduce the protein transmission. They concluded that a thinner cake resulted in a higher filtration rate and a higher protein transmission. The cross-flow microfiltration of the suspension of bentonite with the presence of macromolecules of BSA, Dextran, and PEG were carried out in the study of Jiraratananon et al.[7] The macromolecules decreased the filtration rate of a bentonite suspension while their rejections were enhanced with the presence of bentonite. The constant-pressure filtration models were also applied to explain the blockings in the operations. Guell et al.[8] studied the effects of yeast cells on the membrane fouling in the microfiltration of protein mixtures. A thicker yeast cake resulted in a lower filtration rate and a lower protein transmission. Recently, Kuberkar and Davis[9] developed a mechanistic model to show how a dynamic membrane formed by large particles could capture small particles. The suspension of yeast–protein mixture was used to test the model. They found that the dynamic membrane formed by yeast could reduce the fouling of primary membrane, and that the presence of yeast increased the total permeate volume by two fold.

Since the actual applications may involve complex process streams or multiple components in the suspensions, to understand the effects of operating conditions on the performance of the microfiltration of multicomponent suspensions is very important. In this article, the effect of the dynamic membrane formed by fine particles on the rejection of macromolecules in cross-flow microfiltration is studied. The filtration rates and the rejections of macromolecules under various operating conditions, such as cross-flow velocity and filtration pressure, are discussed.

THEORY

Rejection of Macromolecules

Suspensions containing fine particles are carried by fluid toward the filter membrane to form a filter cake or a concentration polarization layer during a cross-flow microfiltration. The filter cake serves as a secondary membrane to retain or reject the macromolecules. The observed rejection of solute macromolecules is defined as

$$R_{rej} = 1 - \frac{C_p}{C_b} \tag{1}$$

where C_p and C_b are the solute concentrations in the filtrate and in the bulk suspension, respectively. Once these concentrations are measured, the observed rejection can be calculated according to Eq. (1).

Filtration Resistances

The overall resistance of a microfiltration is determined by the cake mass, the concentration profile of particles near the filter membrane or the cake structure, the filtration resistance of membrane, and the blocking of membrane pores. Therefore, the basic cake filtration equation can be written as

$$q = \frac{\Delta P}{\mu(R_t)} = \frac{\Delta P}{\mu(R_c + R_{if} + R_m)} \tag{2}$$

where q is the filtration rate, ΔP is the filtration pressure, μ is the viscosity of fluid, and R_t, R_c, R_{if}, and R_m are the overall filtration resistance, the cake resistance, the filtration resistance due to the internal fouling in the membrane pores, and the clean membrane resistance, respectively. The values of R_t can be calculated from the data of filtration rates using Eq. (2) while R_m from the pure water flux before filtration. When a filtration is terminated at the preset time, the values of R_c and R_{if} can be obtained from the clean water flux before and after the membrane cleaning. For example, after removing the filter cake, the value of R_{if} can be obtained from the difference between the filtration resistance of the fouled membrane and R_m.

In general, the filtration resistance of concentration polarization can be neglected in the condition of a cake formation. However, this resistance can be estimated using the similar experimental method mentioned above if it is necessary. Since the concentration polarization layer will be swept away by

changing the suspension to pure water under the same cross-flow velocity and filtration pressure during a filtration, the filtration resistance of concentration polarization can therefore be obtained from the difference between the fluxes before and after the change.

In the initial stage of filtration, membrane fouling may be dominated by internal fouling. The blocking filtration model[10] can be used to describe the attenuation of filtration rate for the case of large R_{if}.

Filtration of Macromolecules Through a Dynamic Membrane

The macromolecules may be captured or rejected by the formed dynamic membrane during filtration. This phenomenon is similar to those in depth filtration. Small particles are adsorbed, retained, or deposited in the thicken filter media. If the dynamic membrane can be treated as a depth filter,[9] the concentration profile of macromolecules can be given by the standard capture equation for depth filtration[11]:

$$\frac{dC}{dx} = -\gamma C \tag{3}$$

where C is the concentration of macromolecules, x is the distance from the membrane surface toward the cake surface, and γ is a screening parameter representing the fraction of macromolecules rejected by the cake per unit depth. Neglecting the concentration polarization above the cake surface and the adsorption of macromolecules in the membrane, Eq. (3) can be integrated subject to $C = C_p$ at $x = 0$ and $C = C_b$ at $x = L$ to yield

$$C_p = C_b \exp(-\gamma L) \tag{4}$$

Substituting Eq. (4) into Eq. (1), the value of rejection can be calculated by

$$R_{rej} = 1 - \exp(-\gamma L) \tag{5}$$

And the cake thickness, L, can be obtained from the material balance of cake

$$L = \frac{w_c}{\rho_s(1-\varepsilon)} \tag{6}$$

Once the cake mass, w_c, the particle density, ρ_s, and the cake porosity, ε, are measured, the rejection of macromolecules can be estimated by Eq.(5).

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EXPERIMENTAL

The polymethly methacrylate (PMMA) spherical particles manufactured by Soken Chemical & Engineering Co. of Japan were used in experiments as the submicron particulate sample. The diameter of the particles was very uniform and had a mean value of 0.25 micrometers. The true density of the particles was 1210 kg/m^3, while their zeta potential was -32 mV as they dispersed in deionized water. Three kinds of Dextran manufactured by SIGMA® Co. were also suspended in deionized water to prepare macromolecular suspensions; they were T70 (MW = 70,000), T500 (MW = 500,000), and T2000 (MW = 2,000,000), respectively. The pH value of the suspension was kept at 6–7 in this study, while the temperature was kept at 20°C using a thermostat. The Durapore membrane made of PVDF with an average pore size of 0.1 μm was used in experiments. As a result, some of the Dextran molecules could permeate through the filter membrane during a filtration, while the PMMA particles could be retained completely by the used membrane.

Cross-flow microfiltration experiments were carried out using the filtration system shown in Fig. 1. The two-parallel-plate microfilter with a filtration area of 1.14×10^{-4} m^2 was used in filtration. The filter channel was with a height of 1.0×10^{-3} m and with a width of 2.0×10^{-3} m. The cross-flow velocity and the filtration pressure were adjusted to the preset values using the control valves.

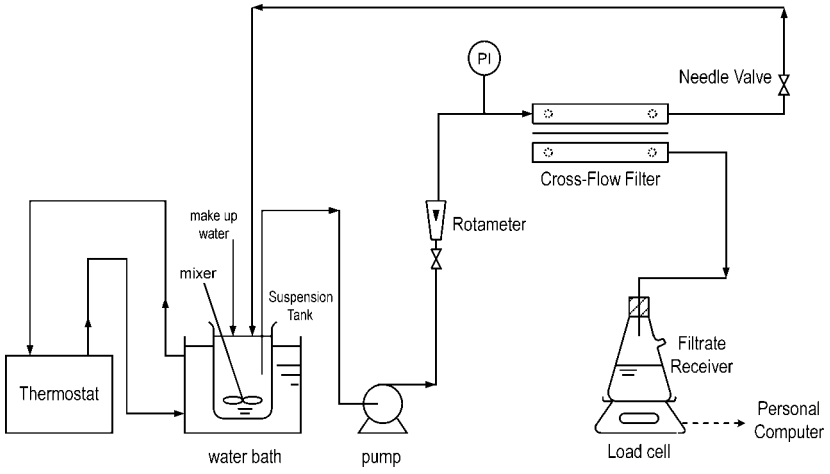

Figure 1. A schematic diagram of cross-flow microfiltration system.

The increase of the weight of the filtrate was detected by a load cell and recorded on a personal computer. The filtration rates were calculated using the data of filtrate volume versus time. The concentration of Dextran in the filtrate was measured by a UV/Visible spectrometer after each time increment of 10 minutes during a filtration. The filtrate sample was diluted and colored by adding a little of phenol. A few drops of concentrate sulfuric acid were added into the solution to dewater from the molecules of Dextran. Then, the concentration of Dextran could be measured accurately using the spectrometer. As soon as the experiment was terminated, the cake formed on the filter membrane was sent to analyze its wet and dry mass by a thermal gravity analyzer. The average porosity and the average specific filtration resistance of the filter cake could be calculated by material balance and the basic filtration equation, respectively. The cross-flow velocity ranged from 0.1 to 0.5 m/s in this study; as a result, the Reynolds number is about 300–800.

RESULTS AND DISCUSSION

The time courses of filtration rates in cross-flow microfiltration of various suspensions are shown in Fig. 2. The initial average cross-flow velocities are 0.18 m/s, whereas as the filtration pressures are 100 kPa for all of the cases in

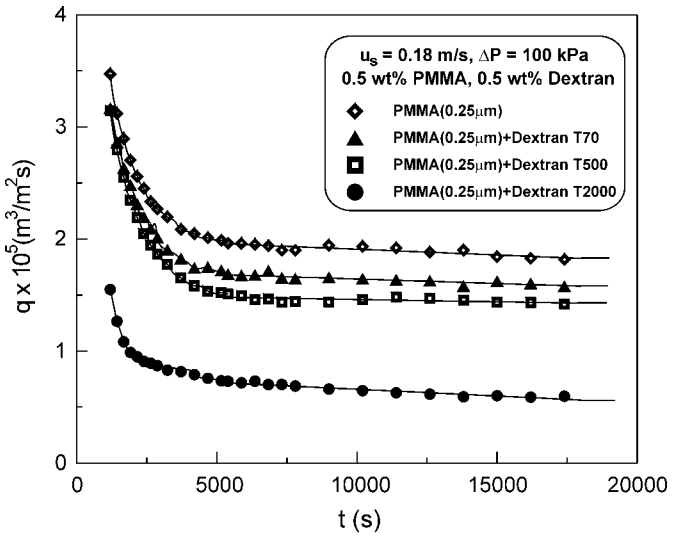

Figure 2. Time courses of filtration rates during cross-flow microfiltration of various suspensions.

this figure. The diamond symbols represent the results of microfiltration of only PMMA suspension; while the others are binary suspensions mixed by different kinds of Dextran and the PMMA particles. It can be found that the filtration rates attenuate quickly at the beginning of filtration due to the formation of cake (dynamic membrane), and then approach to pseudo-steady values when the filtration times exceed 6000 seconds. This tendency is the same as most results in the previous researches. Since Dextran is a kind of polysaccharides, the long and flexible chains of Dextran molecules may be adsorbed on the surfaces of PMMA particles or in the membrane pores during filtration. Consequently, the presence of Dextran in the suspension decreases the filtration rate. In addition, an increase in the molecular weight of Dextran causes the filtration rate to be lower. This is because larger molecules have more opportunities to be captured or rejected by the dynamic membrane. The viscosities of filtrates for three kinds of Dextran were measured at the same operating temperature after experiments. The difference of viscosity between the filtrate and pure water is less than 5% under such low macromolecular concentration, and the variation of viscosity due to molecular weight can be neglected.

In order to understand the role of dynamic membrane in cross-flow microfiltration of macromolecules, the filtration resistances from various sources are analyzed and are shown in Figs. 3 and 4. Figure 3 shows the filtration resistances at the pseudo-steady state in cross-flow microfiltration under various filtration pressures. It can be found that the filtration resistances of the clean membrane and the internal fouling in membrane pores are negligible small compared to the filtration resistance of cake. The filtration resistance of cake plays the major role in the filtration rate, and its value increases with increasing filtration pressure due to more cake formation. The effect of cross-flow velocity on the filtration resistances is illustrated in Fig. 4. The results also show that the filtration resistance of cake is far larger than the other filtration resistances within the operating conditions of this study. Since the cake mass decreases with the increase of cross-flow velocity due to a larger shear stress acting on the cake or the membrane surface, an increase in the cross-flow velocity causes the overall filtration resistance to decrease. Moreover, the values of R_{if} shown in Figs. 3 and 4 demonstrate that a more series blocking of membrane occurs under a higher filtration pressure or a lower cross-flow velocity. These results agree with those in previous studies on membrane blocking[10]; however, the impact of R_{if} on the overall filtration resistance is only 5%.

The properties of the dynamic membrane are measured in this study. Figure 5 shows the masses and the porosities of cakes formed under various cross-flow velocities. An increase in cross-flow velocity leads the cake mass to

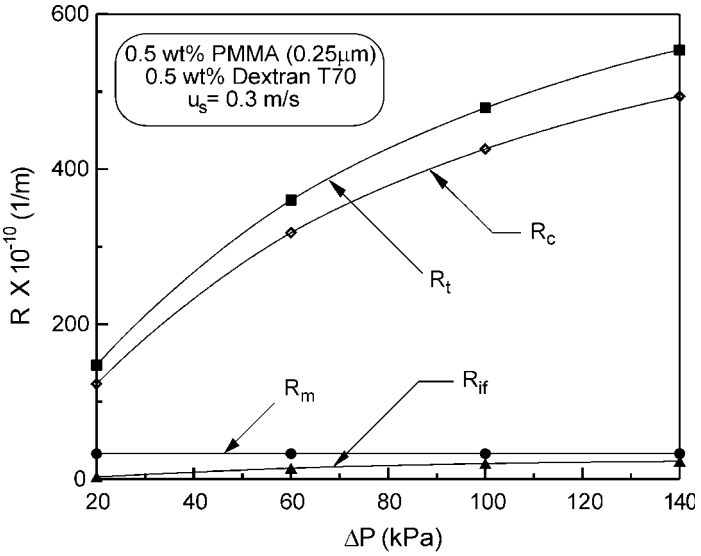

Figure 3. Effect of filtration pressure on the filtration resistances from various sources.

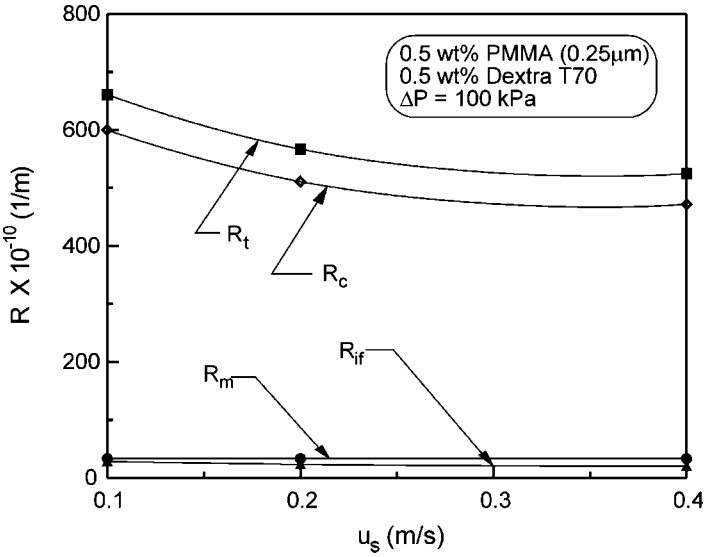

Figure 4. Effect of cross-flow velocity on the filtration resistances from various sources.

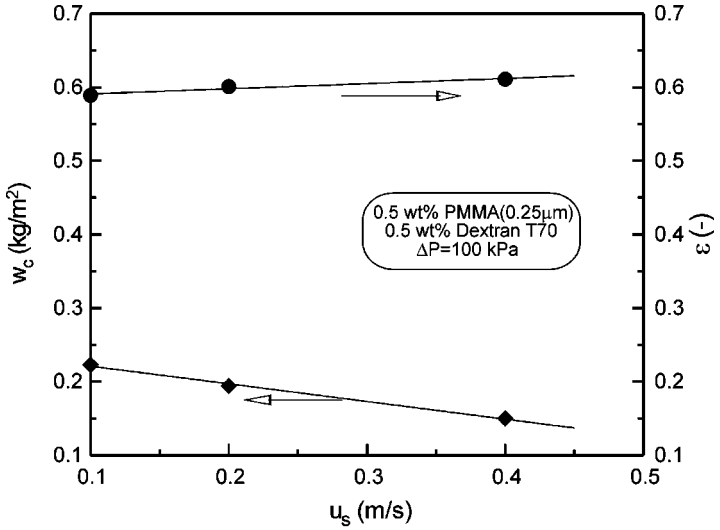

Figure 5. Effects of cross-flow velocity on the mass and the porosity of cake.

decrease but the cake porosity to increase slightly. These are because the higher shear stress limits the growth of cake and results in a different packing structure of particles. These tendencies are the same as those in cross-flow filtration of fine particles.[3] From the results shown in Fig. 5, it can be expected that a thinner or a looser cake will be formed under a higher cross-flow velocity due to higher shear stress acting on the membrane surface.

Figure 6 shows the time courses of filtration rates in cross-flow microfiltration of binary suspensions under various filtration pressures. The tendency of each curve is the same as those in Fig. 2. The filtration rate decays quickly at the beginning of filtration and then approaches to a pseudo-steady value. An increase in filtration pressure causes the filtration rate to increase due to a larger driving force of filtration regardless of more cake formation. The effects of filtration pressure and cross-flow velocity on the pseudo-steady filtration rates are illustrated in Fig. 7. The symbols shown in the figure are experimental data, while the curves are regressed results. An increase in cross-flow velocity leads to a thinner cake (see Fig. 5) and therefore to a higher filtration rate. In addition, the pseudo-steady filtration rate can be regressed to linear functions of cross-flow velocity and filtration pressure within the operating conditions of this study.

The Dextran molecules may be retained in part by the dynamic membrane formed by PMMA particles during a microfiltration. In order to understand

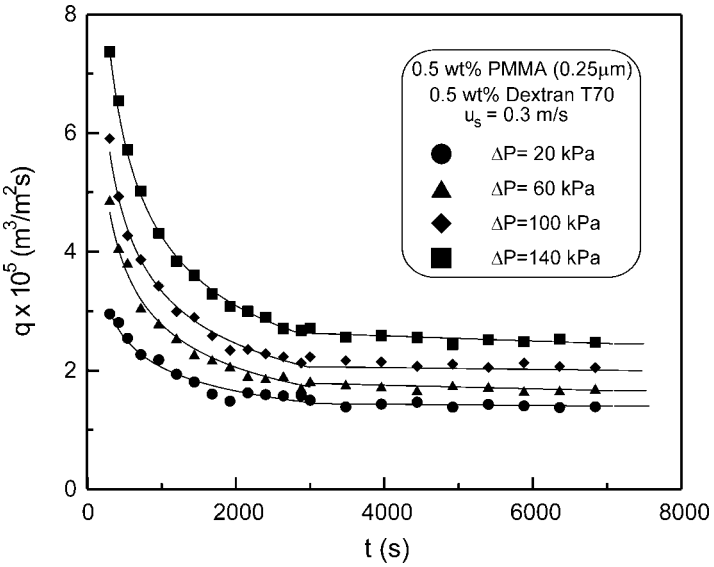

Figure 6. Time courses of filtration rates during cross-flow microfiltration of binary suspension under various filtration pressures.

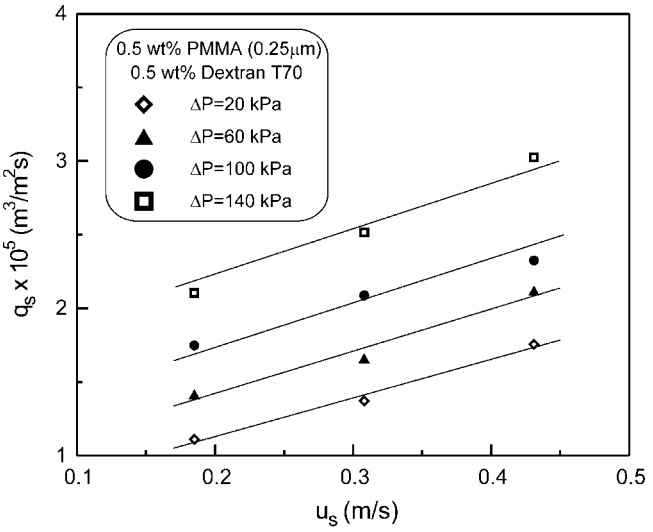

Figure 7. Effects of cross-flow velocity and filtration pressure on the pseudo-steady filtration rates.

the role of dynamic membrane in this kind of filtration, the rejections of Dextran under various operating conditions are measured in experiments. Figure 8 depicts the time courses of the observed rejection of Dextran during cross-flow microfiltration under various filtration pressures. The value of rejection increases quickly within the first 60 minutes of filtration. However, when the operation approaches a pseudo-steady state, the value of rejection remains a constant for the time being. The variations of rejection during filtration are similar to those in "dead-end" microfiltration of previous studies.[6,8] From the results of previous works[6,8] and those in this study, a strong effect of the formed cake on the rejection of macromolecules can be inferred regardless of the filtration modes. Moreover, from the results shown in Fig. 8, a higher filtration pressure results in a higher rejection of Dextran due to more cake mass formed.

From Eqs. (5) and (6), one knows that the mass and the porosity of the dynamic membrane are the important factors to determine the rejection of macromolecules. However, the compressibility of the cake formed by PMMA particles is small, the variations of the cake porosity under various conditions are also negligible small. This fact can be found in Fig. 5. The values of Dextran rejection are plotted in Fig. 9 against the cake masses under different filtration times and under various cross-flow velocities. Although the data was

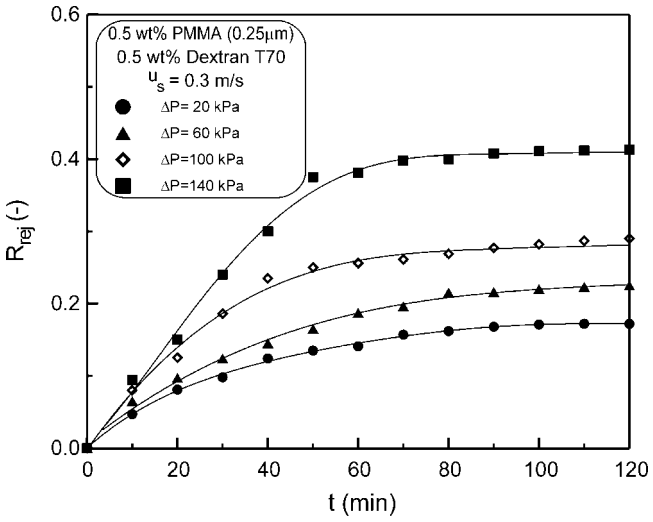

Figure 8. Variations of observed rejection of Dextran during cross-flow microfiltration of binary suspension under various filtration pressures.

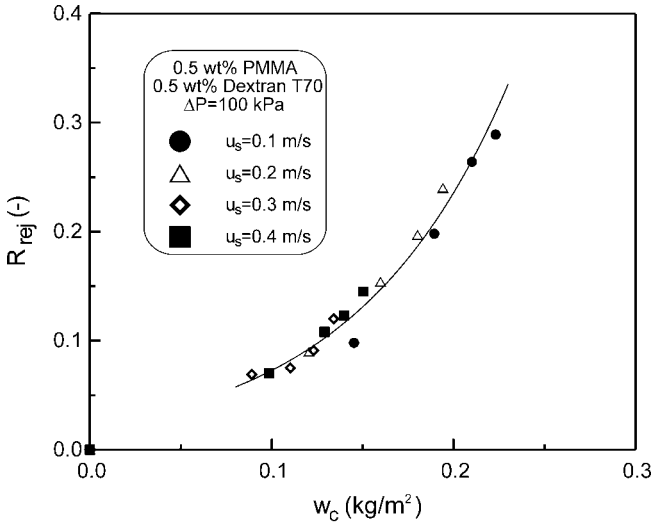

Figure 9. The relationship between the rejection of Dextran and the mass of cake formed by PMMA particles.

measured under various operating conditions, they can be regressed to a single curve. This result implies that the cake mass is the most important factor on the rejection of Dextran within the operating conditions of this study. This figure also shows that the values of rejections increase with increasing the cake mass, and the rejection of macromolecules will increase due to the presence of fine particles. These results are similar to those in "dead-end" microfiltration.[6] Therefore, the optimum operating condition can be determined once the masses of dynamic membrane under various conditions are known or estimated.

The effects of filtration pressure and cross-flow velocity on the pseudo-steady values of observed rejections of Dextran are shown in Fig. 10. Although a higher pseudo-steady filtration rate is obtained under a higher filtration pressure, the larger amount of the formed cake causes the rejection of Dextran to be higher. Furthermore, a higher cross-flow velocity leads to a thinner cake. As a result, a lower rejection of Dextran is obtained. These results demonstrate that the mass of dynamic membrane plays the most important role on the observed rejection of Dextran.

If the dynamic membrane can be treated as a depth filter to capture macromolecules, Eq. (5) can be employed to relate the rejection of Dextran and the thickness of dynamic membrane. Figure 11 is a semi-log plot of

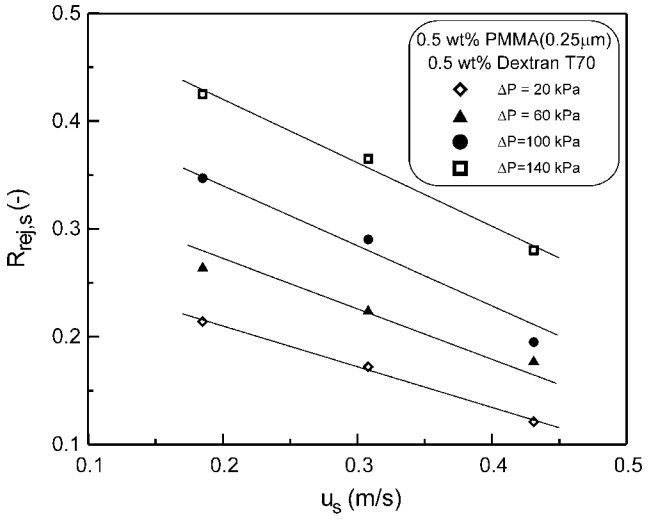

Figure 10. Effects of cross-flow velocity and filtration pressure on the pseudo-steady rejection of Dextran.

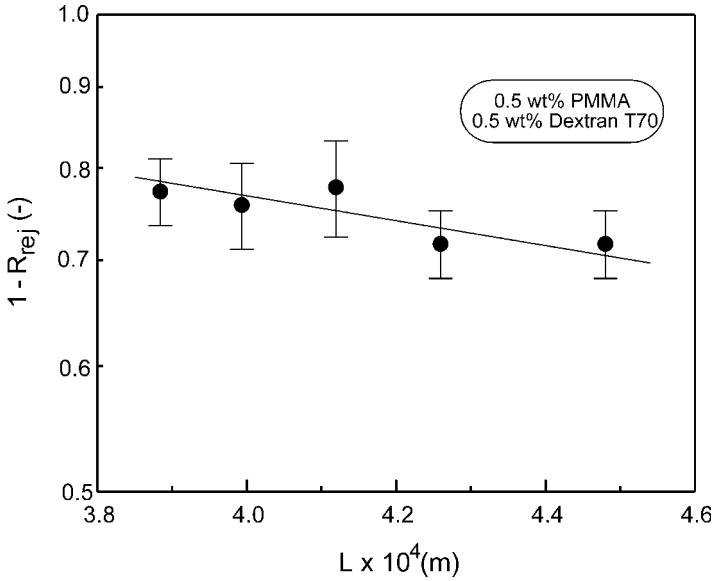

Figure 11. A plot of $1 - R_{rej}$ versus L.

$1 - R_{rej}$ versus L, in which the values of L are calculated using Eq. (6). The experimental data shown in this figure can be regressed as a straight line; therefore, the screen parameter, γ, can be obtained from the slope of the line. Since the value of γ is a constant within the operating conditions in this study, it implies that the filtration rate and the adsorption of Dextran on the particle surfaces have less effect on the screening parameter. The results imply that the rejection of macromolecules can be determined using the standard capture equation, Eq. (5).

CONCLUSIONS

The effects of operating conditions on the filtration rates and the rejections of macromolecules in the cross-flow microfiltration of binary suspensions have been studied. The filtration rate increased with increasing the cross-flow velocity and the filtration pressure, but decreased with increasing the molecular weight of Dextran. On the other hand, the rejection of Dextran increased with the increase of filtration pressure but decreased with the increase of cross-flow velocity. The standard capture equation for deep-bed filtration could be used to relate the rejection of Dextran and the properties of dynamic membrane. The mass of the dynamic membrane was the major factor on the rejection of Dextran within the operating conditions of this study. Using the experimental data obtained under various cross-flow velocities, the rejection of Dextran could be regressed as a single function of the cake mass. The rejection of macromolecules would increase due to the presence of fine particles, and the value of rejections increased with increasing the cake mass.

NOMENCLATURE

C	concentration of solute molecules (kg/m^3)
C_b	concentration of solute molecules in bulk suspension (kg/m^3)
C_p	concentration of solute molecules in filtrate (kg/m^3)
L	thickness of secondary membrane (cake) (m)
ΔP	filtration pressure (N/m^2)
q	superficial velocity of filtrate or filtration rate ($m^3/m^2\,s$)
q_s	pseudo-steady filtration rate ($m^3/m^2\,s$)
R_c	filtration resistance of cake (m^{-1})

R_{if}	filtration resistance due to internal fouling in membrane pores (m^{-1})
R_m	filtration resistance of membrane (m^{-1})
R_{rej}	observed rejection of macromolecules (−)
$R_{rej,s}$	observed rejection of macromolecules at pseudo-steady state (−)
R_t	overall filtration resistance (m^{-1})
t	filtration time (s)
u_s	average cross-flow velocity at the inlet of filter (m/s)
w_c	mass of dry cake per unit area (kg/m^2)
x	distance from the membrane surface toward the cake surface (m)

Greek Letters

ϵ	average cake porosity (−)
γ	a screening parameter (m^{-1})
μ	viscosity of liquid (kg/s m)
ρ_s	density of particles (kg/m^3)

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