ELSEVIER

Separation and Purification Technology 00 (2002) 1–9

Separation and Purification Technology

www.elsevier.com/locate/seppur

Effect of electrostatic repulsive force on the permeate flux and flux modeling in the microfiltration of negatively charged microspheres

Sung-Wook Choi [a], Jung-Min Park [a], Yongsu Chang [a], Jeong-Yeol Yoon [b], Seungjoo Haam [c], Jung-Hyun Kim [a], Woo-Sik Kim [a,*]

[a] *Nanosphere Process and Technology Laboratory, Department of Chemical Engineering, Yonsei University, 134 Shinchon-dong, Sudaemoon-ku, Seoul 120-749, South Korea*

[b] *Department of Chemistry and Biochemistry, Biomedical Engineering IDP, University of California, Los Angeles, CA 90095, USA*

[c] *Fluid Mixing Technology Laboratory, Department of Chemical Engineering, Yonsei University, 134 Shinchon-dong, Sudaemoon-ku, Seoul 120-749, South Korea*

Received 21 February 2002; received in revised form 21 June 2002; accepted 21 June 2002

Abstract

A study on the permeate flux was performed in a stirred cell filled with monodispersed carboxylated microspheres (polystyrene/polymethacrylic acid, PS/PMAA), to investigate the effects of surface charge (the number density of surface carboxyl group, N_c; 0.45, 5.94, 9.14, and 10.25 nm^{-2}) and the stirrer speed (300, 400, and 600 rpm) under constant transmembrane pressure. The permeate flux was found to be dependent on the surface charge, the ionic strength, and the stirrer speed. The permeate flux was proportional to the surface charge of microspheres and inversely proportional to the ionic strength because of electrostatic repulsive interaction and steric hindrance. The cake porosity was estimated by Kozeny–Carman equation from the steady-state permeate flux data. Experimental data elucidated that the cake porosity was extended from 0.211 to 3.04 upon the introduction of carboxyl group on the microsphere surface, leading to the high permeate flux. Consequently, resistance-in-series model was employed for the modeling of the permeate flux and showed a good agreement with the experimental results. © 2002 Published by Elsevier Science B.V.

Keywords: PS/PMAA microspheres; Permeate flux; The number density of surface carboxyl group; Electrostatic interaction; Resistance-in-series model

Nomenclature

A	area (m^2)
d	diameter (m)

* Corresponding author. Tel.: +82-2-2123-2753; fax: +82-2-312-0305
E-mail address: choisw94@empal.com (W.-S. Kim).

1383-5866/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S1383-5866(02)00121-1

$J(t)$	permeate flux (m s^{-1})
k	rate of cake formation (s^{-1})
m	total dried mass of a cake layer (kg)
N	the number density of surface carboxyl group (nm^{-2})
R	resistance (m^{-1})
t	filtration time (s)
V	total volume of permeate
ΔP	transmembrane pressure (Pa)
z	distance (m)

Greek letters

ε	cake porosity (dimensionless)
κ	Debye–Hückel parameter (m^{-1})
μ	dynamic viscosity (Pa·s)
ρ	density (kg m^{-3})
ψ	surface potential (mV)

Subscripts

c	cake layer (in R_c) or carboxyl group (in N_c)
m	Membrane
p	particle (in d_p) or permeate (in V_p)

Superscript

*	in steady-state

1. Introduction

Membrane filtration has a great potential for removing colloidal suspensions such as clay particles, proteins, and other macromolecules. However, the major obstacle in membrane filtration is the flux decline due to the concentration polarization and the fouling. During filtration of colloidal suspensions, particles are driven onto the membrane surface where they accumulate and form a cake or gel layer. This particle build-up is known as a concentration polarization, and results in increasing of the hydraulic resistance to permeate flux.

Many researchers have studied on the variation and modeling on the flux decline. Bhattacharjee [1] had developed the predictive model for the flux decline in unstirred and stirred batch cells by unifying the osmotic pressure and gel layer model. These analyses were mostly suitable for the filtration of an aqueous solution of low molecular weight solutes (osmotic pressure controlled) and high molecular weight solutes (gel layer controlled). A force balance model was also developed to predict the effects of particle size, particle size distribution, and surface potential on the structure of the cake layer [2]. Crossflow filtration of monodispersed polystyrene latex ranging from 0.064 to 2.16 μm in diameter was studied under constant transmembrane pressure mode by Lee and Clark [3]. Besides the crossflow filtration tests, dead-end filtration test were also carried out to independently determine a model parameter, the specific cake resistance. Benkahla et al. [4] studied on the fouling mechanism in filtration of a mineral $CaCO_3$ suspension using Ergun's equation and Darcy's law. Hamachi [5] has used a conventional crossflow microfiltration pilot with a laser device

to measure deposit thickness and studied on the effect of accumulative volume, time, and transmembrane pressure on the thickness of deposition.

There were several studies [2,6,7] about the influence of surface interaction on permeate flux. McDonogh et al. [6] conducted cross-flow ultrafiltration experiments using non-flocculating silica particles. They studied the charge effect of the particles and the retentate permeability on membrane performance. Bacchin [7] reported that the critical flux of clay suspensions decreased to zero by adhesion as increasing the salt concentration. The reduction of surface repulsive force was responsible for such changes. These researches generally adjusted the repulsive force of particle by controlling ionic strength, pH, and salt concentration. In this paper, however, the charge effect of microsphere itself was mainly investigated on the permeate flux. The surface charges of microspheres with same particle size were varied by co-polymerization of styrene and methacrylic acid.

This paper is focused on the effect of surface charge of polystyrene/polymethacrylic acid microspheres (PS/PMAA) on the flux behavior and the modeling of permeate flux by resistance-in-series equation. These results were used for the basic data for the protein separation systems previously proposed in our group [8]. In the first section, the surface charge effect of microspehres on the flux behavior was studied in various conditions (the number density of surface carboxyl group, stirrer speed, ionic strength). In the second part, these experimental results were fitted to the theoretical model. From these analyses, the cake porosity and the flux behavior were studied in detail.

2. Experiment

2.1. Materials

Styrene (St) and methacrylic acid (MAA) were from Junsei Chemical Co. (Japan) and used as monomers for the copolymerization after a purification with Aldrich's inhibitor remover column (catalog number 306312). Potassium persulfate (KPS, Samchun Pure Chemical Ind., Ltd., Korea) was used as an initiator for co-polymerization. Synthesized microspheres were purified by mixed-bed ion exchange resins (Dowex MR-3, Sigma Chemical Co., USA, catalog number I-9005). An acetic buffer of pH 4.5 was made of sodium acetate and acetic acid (both from Yakuri Pure Chemicals Co., Ltd., Japan). A polyether sulfone (PES) planar membrane (Orange Scientific Co., Belgium) with pore size of 0.2 μm was used for the microfiltration study. All water used in the experiments was distilled and deionized, produced by Elgastat's UHQ system (UK).

2.2. Preparation and characterization of microspheres

St and MAA were used as a main monomer and co-monomer, respectively, where the surface carboxyl group will be given by hydrophilic MAA. Soap-free emulsion polymerization was preformed in a 1.5 l internally stirred jacketed reactor at 70 °C, and nitrogen gas was purged in small doses to provide nitrogen atmosphere. Low carboxylated microsphere (CM-1) was prepared by batch copolymerization and highly carboxylated ones (CM-2, 3, and 4) were prepared by the two stage shot growth method [9]. Tables 1 and 2 give the recipes for the synthesis of PS/PMAA microspheres with various number density of surface carboxyl group.

The microspheres were purified by mixed-bed ion-exchange resins and further purified by serum replacement method [10]. The serum replacement procedure was performed in a 400 ml stirred cell (Amicon, Model 8400, USA) equipped with 0.2 μm membrane filters. The particle diameter of microspheres was assessed by Scanning Electron Microscopy (JEOL, Japan) and the number density of surface carboxyl groups was determined

Table 1
Recipe for the low carboxylated PS/PMAA microspheres (batch copolymerization)

	St (g)	MAA (g)	KPS (g)	D.D.I. water (g)
CM-1	60	0.6	0.24	600

Table 2
Recipe for the highly carboxylated PS/PMAA microspheres (two stage shot growth method) [9]

First stage		Second stage (injected at conversion 90%)		
St (g)	60	CM-2	MAA	1.5 (g)
MAA (g)	0.6	CM-3	MAA	3.0 (g)
KPS (g)	0.24	CM-4	MAA	6.0 (g)
D.D.I Water (g)	600			

using conductivity meter (HI 8633 conductivity meter, Portugal) using NaOH solution as a titrant.

2.3. Procedure of microfiltration

The experimental set-up is schematically shown in Fig. 1. A stirred cell (50 ml, Amicon, model 8050, USA) with a 0.2 μm membrane filter (Orange Scientific Co., Belgium) was filled with 30 ml disperstion of microspheres (0.47 g microspheres per 30 ml). The specific surface area was 0.19 m^2 per 1 ml and the ionic strength was 0.01, which were the same conditions of our previous studies [11]. At a constant stirrer speed, acetic buffer (pH 4.5) was introduced into the stirred cell until the permeate flux was in steady state. The permeate flux was continuously measured with an electronic balance (precision plus, Ohaus Co., USA). The electronic balance was connected to a PC through a RS 232 C interface. The number density of surface carboxyl group (N_c) of microspheres was varied as 0.45, 5.94, 9.14 and 10.25 nm^{-2}, and the stirrer speed was varied as 300, 400 and 600 rpm. The filtration of pure water without microsphere was performed to determine membrane resistance (R_m). All experiments were conducted in three times.

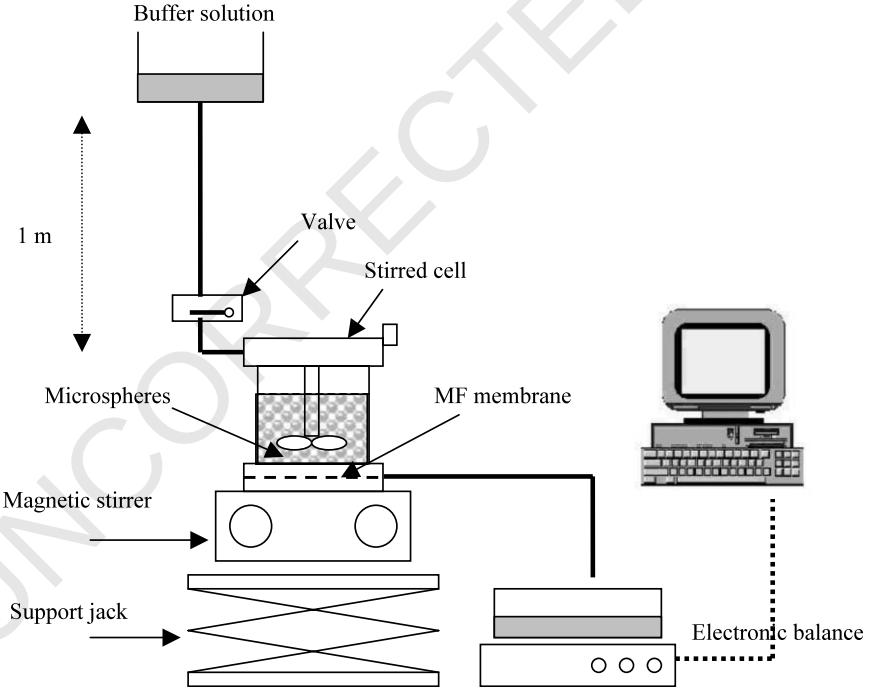

Fig. 1. Experimental apparatus for microfiltration.

Table 3
Characterization results of the various monodisperse microspheres

	CM-1	CM-2	CM-3	CM-4
d_p (nm)	478	481	480	485
N_c (nm^{-2})	0.45	5.94	9.14	10.25

3. Results and discussion

The particle size and the number density of surface carboxyl group of various microspheres are shown in Table 3. All microspheres have a polydispersity index near unity (1.009 determined by Capillary hydrodynamic Factionation, CHDF-1100, Matec Applied Sciences, USA) and the same particle size to investigate the effect of surface charge only.

3.1. Study on the steady-state permeate flux

The permeate flux initially decreased with time due to the formation of a cake layer during microfiltration and then reached steady state. Fig. 2 shows the steady-state permeate flux with respect to the number density of surface carboxyl group and stirrer speed. The faster the stirrer speed, the higher the permeate flux because of the high shear stress at the surface of a cake layer. The permeate flux was found to be increased with N_c, because the high repulsive force resulted in the increase of effective radii of microspheres. Therefore, the larger cake porosity and steric hindrance could be achieved, leading to the large permeate flux. The change of the cake porosity was calculated by resistance-in-series model (results shown in Section 3.2). Fig. 3 gives the schematic explanation of the effect of surface charge on the permeate flux.

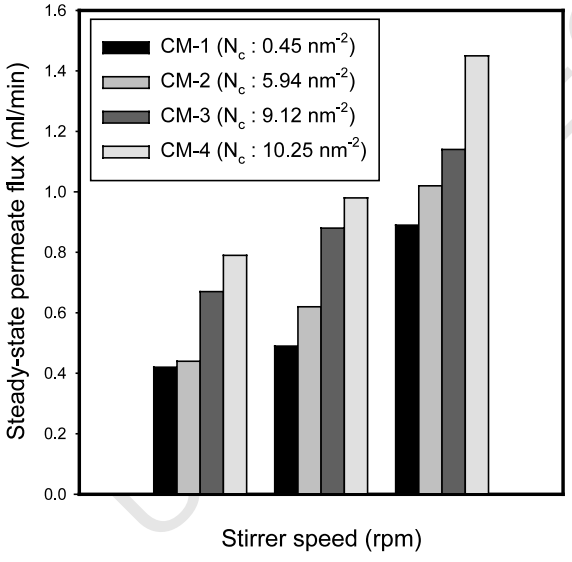

Fig. 2. Steady-state permeate flux with different stirrer speeds and the number densities of surface carboxyl group.

Fig. 4 shows the permeate flux of CM-4 through membrane at stirrer speed of 400 rpm with respect to the ionic strength. The high ionic strength (0.1) results in decreased thickness of electric double layer. The electrical potential exponentially decreases over the distance from surface according to the following Debye–Hückel approximation [12,13];

$$\psi = \psi_o \exp(-\kappa z) \quad (1)$$

where ψ, surface potential at distance z (mV); ψ_o, surface potential (mV); κ, the Debye–Hückel parameter (m^{-1}) and z, distance (m).

The parameter κ is directly related to the electrolyte concentration and identified as reciprocal of the thickness of the electrical double layer. Upon decreasing the ionic strength, the thickness of electrostatic double layer around the particle surface increases, leading to the increased permeate flux. It was reported that permeate flux in crossflow filtration (or dead-end filtration) was decreased at a higher ionic strength condition,

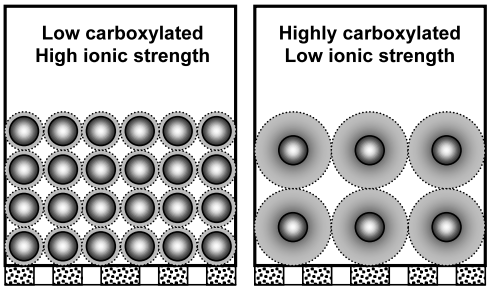

Fig. 3. Schematic diagram illustrating the effect of surface charge on permeate flux.

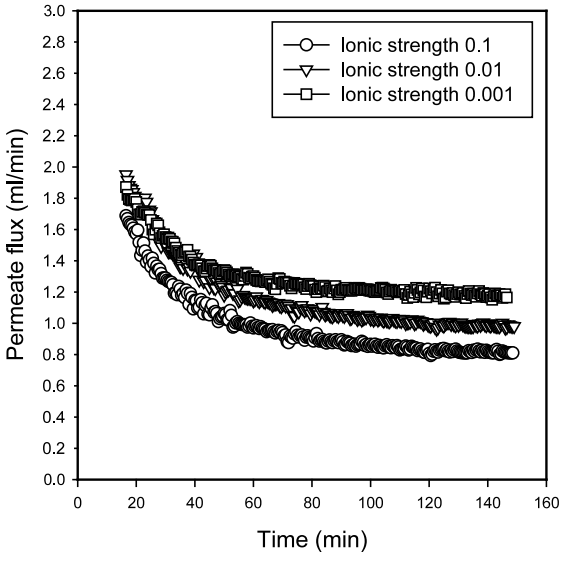

Fig. 4. Effect of ionic strength on the permeate flux with time in CM-4 ($N_c = 10.25\ nm^{-2}$, at 400 rpm).

because the decreased Debye screening length with increasing ionic strength resulted in a denser cake layer [14,15]. As a consequence, the increase of the ionic strength results in a compressed cake layer.

3.2. Cake porosity

The cake porosity was closely related to the surface charge of microspheres and can be estimated from the steady-state flux data using Kozeny–Carman equation and resistance-in-series model. There are two unknown variables such as the total mass of a cake layer (m_p) and the cake porosity (ε).

The total particle mass of a cake layer which mainly depends on the stirrer speed, can be determined as follows [11]; The permeate concentration of microsphere was nearly zero because the membrane pore size was small enough to retain all microsphere in our system. The concentrations were indirectly measured by UV spectrophotometer (UV-160A, Shimadzu, Japan). There was a linear relationship between concentration of microsphere and absorbance. When the permeate flux was in the steady state, the absorbance of retentate was measured. The absorbance of retentate was measured when the permeate flux has reached the steady state. The total particle mass of a cake layer was inversely proportional to the stirrer speed, because increased stirrer speed caused the thickness of a cake layer to decrease. Lee and Clark [3] demonstrated that the specific cake resistance ($= 180(1-\varepsilon)/d_p^2\varepsilon^3$) remained fairly constant during dead-end filtration in the condition of complete rejection, which implying constant cake porosity as assumed.

The cake porosity obtained from the steady-state flux, is plotted against N_c in Fig. 5. The cake porosity was observed to be increased with N_c. The increase of effective radii of microspheres was responsible for the large cake porosity. Similar interpretation was used in the other researches [6,16]. Chang et al. [16] reported that the permeate flux decreased with the increase of the electrolyte concentration of the suspension. This can be explained by assuming both the interparticle distance and repulsive force to be decreased with the higher electrolyte concentration.

When the particle size of uncharged polystyrene microsphere was 480 nm, the cake porosity was 0.211, which was calculated from the empirical equation reported by the Lee and Clark [3]. However, it can be extended by an introduction of carboxyl group on the microsphere surface. If

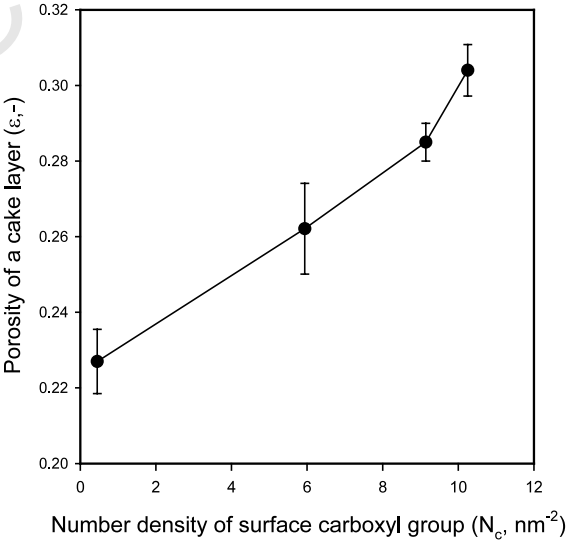

Fig. 5. Calculated cake porosity with the number density of surface carboxyl group.

the surface of microsphere is fully modified with methacrylic acid (in the case of CM-4), the cake porosity is 0.304. The cake porosity was significantly dependent on the thickness of electric double layer (or the effective radius of the particle), which could be varied by the number density of surface carboxyl group and ionic strength.

3.3. Modeling of the permeate flux

Two parameters are required for modeling of the permeate flux; the cake porosity (ε) and the total dried mass of a cake layer (m_p) (determined in Section 3.2.), assumed to be dominantly affected by surface charge of microspheres and stirrer speed, respectively. Resistance-in-series model was employed for the modeling of the permeate flux. In our system, the permeate concentration of microsphere was nearly zero because the membrane pore (200 nm) size was small enough to retain all microspheres (480 nm). Therefore, total resistance is the sum of the membrane and cake resistance. The permeate flux (J) can be expressed as follows,

$$J(t) = \frac{1}{A_m}\frac{dV_p}{dt} = \frac{\Delta P}{\mu(R_m + R_c)} \quad (2)$$

where $J(t)$, permeate flux (m s^{-1}); V_p, total volume of permeate; A_m, membrane area (m^2); ΔP, transmembrane pressure (Pa); μ, dynamic viscosity (Pa·s); R_m, membrane resistance (m^{-1}) and R_c, cake resistance (m^{-1}). R_m can be evaluated from the flux measurement of pure water. From Kozeny–Carman equation, cake resistance can be written as follows

$$R_c = 180\frac{(1-\varepsilon)^2}{d_p^2\varepsilon^3}\frac{m_p}{(1-\varepsilon)A_m\rho_p} = \frac{180(1-\varepsilon)m_p}{d_p^2\varepsilon^3 A_m\rho_p} \quad (3)$$

where m_p, total dried mass of a cake layer (kg); d_p, particle diameter (m); ρ_p, density of particle (kg m^{-3}) and ε, cake porosity (–).

For the modeling of permeate flux, total dried mass of a cake layer should be defined as the function of time and may be written as following equation.

$$m_p(t) = m_p^*(1 - \exp(-kt)) \quad (4)$$

m_p^* is the total dried mass of a cake layer in the steaty-state permeate flux and k is the rate of cake formation. Similar equation was used by Gekas et al. [17]. Therefore, cake resistance can be expressed as follows,

$$R_c = \frac{180(1-\varepsilon)m_p^*(1-\exp(-kt))}{d_p^2\varepsilon^3 A_m\rho_p} \quad (5)$$

The cake porosity was determined from the flux data in steady-state, and this is a key factor to the permeate flux. The cake porosity can be assumed to be constant during filtration [3] and the total dried mass of a cake layer (m_p^*) was a function of stirrer speed and time. The k value can be obtained by a non-linear regression from experimental flux data. The other necessary parameters were as follows: dynamic viscosity (μ) = 0.001 Pa·s, membrane area (A_m) = 0.00134 m^2, particle density (ρ_p) = 1.05 kg m^{-3}, and membrane resistance (R_m) = 1.62×10^8 m^{-1}. The experimental results were compared with the modeling results in Figs. 6–8. The modeling results of the permeate

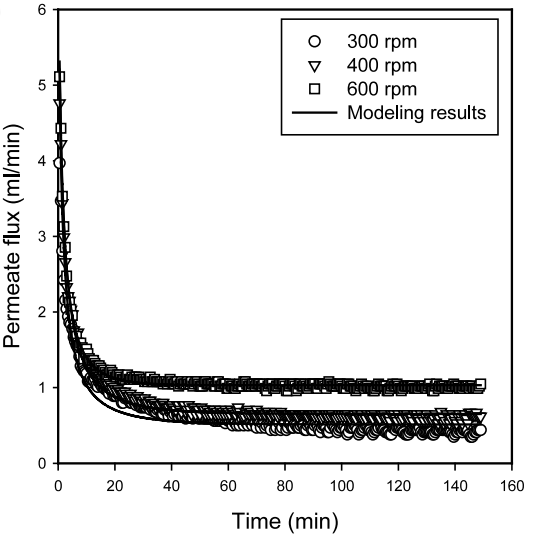

Fig. 6. Comparison of modeling results with experimental data in CM-2 (N_c = 5.94 nm^{-2}).

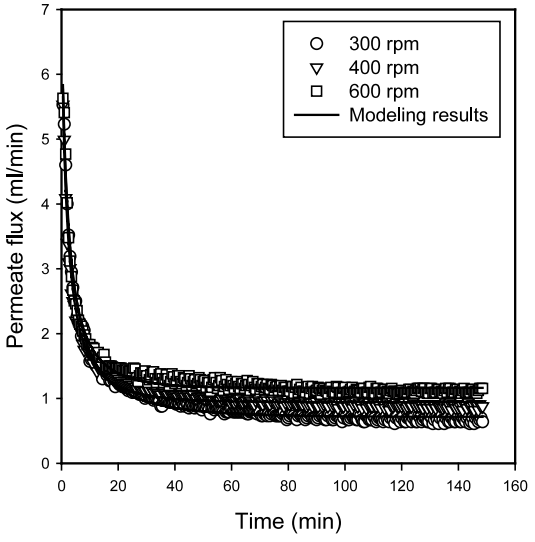

Fig. 7. Comparison of modeling results with experimental data in CM-3 ($N_c = 9.12$ nm^{-2}).

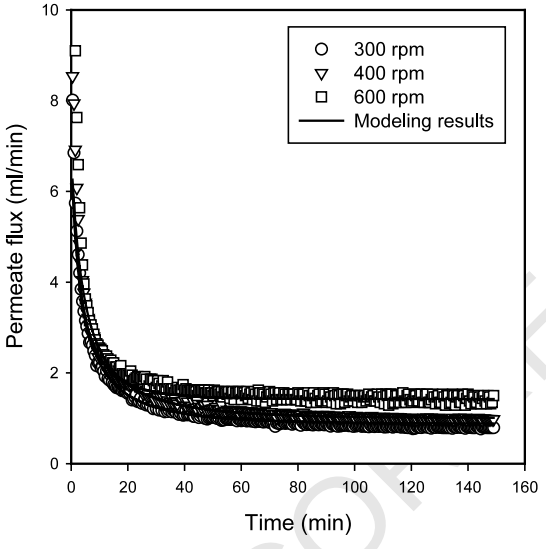

Fig. 8. Comparison of modeling results with experimental data in CM-4 ($N_c = 10.25$ nm^{-2}).

flux were in a good agreement with the experimental data.

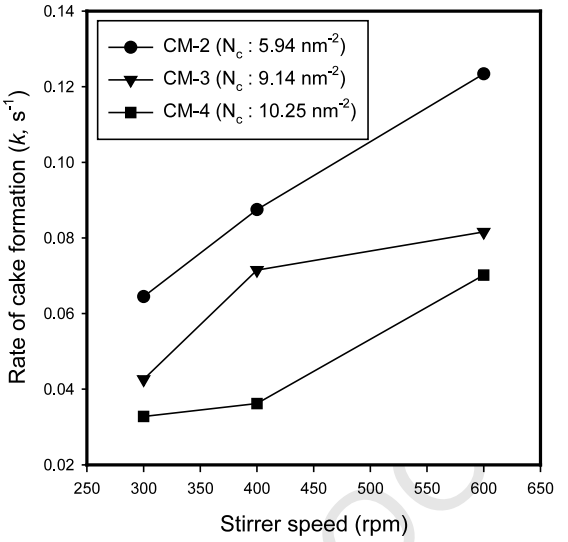

Fig. 9. The rate of cake formation at different stirrer speeds and the number densities of surface carboxyl group.

3.4. Behavior of the permeate flux

The exact evaluation of the rate of cake formation, k, is essential for the flux modeling because the cake formation depends on the particle deposition onto the membrane surface. Fig. 9 shows the rate of cake formation with different stirrer speeds and the number densities of surface carboxyl group. The rate of cake formation was inversely proportional to N_c under constant stirrer speed. The increased N_c leads to a higher permeate flux and a longer time to equilibrate. This means that the cake layer is slowly formed in the filtration of microspheres with high surface charge, due to the repulsive force between microspheres. This phenomenon was due to the interparticle repulsion. The rate of cake formation was found to be increased with the stirrer speed in the same N_c condition, because the microspheres were rapidly accumulated onto the surface of membrane when the permeate flux was high. Consequently, large k value was observed when the microspheres with low surface charge was filtrated in the condition of high stirrer speed.

4. Conclusion

The effect of surface charge on the permeate flux was studied in the microfiltration using stirred cell filled with PS/PMAA microspheres. To obtain large permeate flux, the high surface charge, low ionic strength, and the high stirrer speed were required. The large cake porosity, which was induced by the increase of N_c and the decrease of ionic strength, was responsible for the large permeate flux. The cake porosity could be estimated from the experimental data at the different number densities of surface carboxyl group. It was extended from 0.211 to 0.304 by introduction of methacrylic acid onto microsphere surface. Resistance-in-series model was employed for the modeling of the flux variation. This model provides a useful tool to understand the effect of the electrostatic repulsive force on the permeate flux.

Acknowledgements

The authors acknowledge the financial support of Bioproducts Research Center (1994S0018), Yonsei University and the Korea Institute of S&T Evaluation and Planning (National Research Laboratory Program, M1-9911-00-0044).

References

[1] S. Bhattacharjee, A. Sharma, P.K. Bhattacharya, A unified model for flux prediction during batch cell ultrafiltration, J. Membr. Sci. 111 (1996) 243.
[2] L.F. Fu, B.A. Dempsey, Modeling the effect of particle size and charge on the structure of the filter cake in ultrafiltration, J. Membr. Sci. 149 (1998) 221.
[3] Y. Lee, M.M. Clark, Modeling of flux decline during crossflow ultrafiltration of colloidal suspension, J. Membr. Sci. 149 (1998) 181.
[4] Y.K. Benkahla, A. Ould-Dris, M.Y. Jaffrin, D. Si-Hassen, Cake growth mechanism in cross-flow microfiltration of mineral suspension, J. Membr. Sci. 98 (1995) 107.
[5] M. Hamachi, M. Mietton-Peuchot, Experimental investigation of cake characteristics in crossflow microfiltration, Chem. Eng. Sci. 54 (1999) 4023.
[6] R.M. McDonogh, C.J.D. Fell, A.G. Fane, Surface charge and permeability in the ultrafiltration of non-flocculating colloids, J. Membr. Sci. 21 (1984) 285.
[7] P. Bacchin, P. Aimar, V. Sanchez, Influence of surface interaction on transfer during colloid ultrafiltration, J. Membr. Sci. 115 (1996) 49.
[8] J.Y. Yoon, J.H. Lee, J.H. Kim, W.S. Kim, Separation of serum proteins with uncoupled microsphere particles in a stirred cell, Colloid. Surf. B 10 (1998) 365.
[9] J.H. Kim, M. Chainey, M.S. El-Aasser, J.W. Vanderhoff, J. Polym. Sci. A 27 (1989) 3187.
[10] M.S. El-Aasser, in: M.S. El-Aasser (Ed.), Advances in Emulsion Polymerization and Latex Technology, vol. 2 (Lecture 3), Emulsion Polymers Institute (Lehigh University), Bethlehem, PA, 1984.
[11] S.W. Choi, J.Y. Yoon, S. Haam, J.K. Jung, J.H. Kim, W.S. Kim, Modeling of the permeate flux during microfiltration of BSA-adsorbed microspheres in a stirred cell, J. Colloids Interf. Sci. 228 (2000) 270.
[12] D. Myers, Surfaces, Interfaces, and Colloids: Principles and Applications, VCH Publishers, New York, 1991, p. 76,.
[13] R. Buscall, T. Corner, J.F. Stageman, Polymer Colloids, Elsevier Applied Science Publishers, New York, NY, 1985, p. 144.
[14] R.S. Faibish, M. Elimelech, Y. Cohen, Effect of interparticle interaction on flux decline in crossflow membrane filtration of colloidal suspensions, Proceedings, Nineth Annual Meeting, North American Membrane Society, Baltimore, 1997.
[15] M.S. Chun, G.Y. Chung, J.J. Kim, On the behavior of the electrostatic colloidal interaction in the membrane filtration of latex suspensions, J. Membr. Sci. 193 (2001) 97.
[16] D.J. Chang, F.C. Hsu, S.J. Hwang, Steady state permeate flux of cross-flow microfiltration, J. Membr. Sci. 98 (1995) 97.
[17] V. Gekas, P. Aimar, J.P. Lafaille, V. Sanchez, A simulation study of the adsorption–concentration polarization interplay in protein ultrafiltration, Chem. Eng. Sci. 48 (1993) 2753.