

Rejection Properties of Silica Nanoparticles from Ultrafiltration Membranes

Hiromitsu Takaba[†], Yoshiaki Ito, and Shin-ichi Nakao

Development of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, JAPAN

(Received December 9, 2003, Accepted December 15, 2003)

Abstract: The rejection properties and flux rates of silica nanoparticles in ultrafiltration membranes has been investigated. Cross-flow permeation experiments were conducted using polycarbonate track-etch flat membranes with pore sizes of 30 and 50 nm, and a silica nanoparticle solute with particle sizes of 5 and 18 nm with narrow size distributions. The fluxes and rejection factors were investigated at various particle concentrations, cross-flow velocities, pH, and ionic strengths of solution. Even though the size of the silica nanoparticles was much smaller than that of the membrane pores, the observed rejection rates were very high compared with those for a similar-sized polymer (dextran). The observed rejection rate decreased with increasing ionic strength, which implies that the transport mechanism of the silica nanoparticles is significantly influenced by electrostatic repulsion between particles and membranes.

Keywords: nanoparticle, ultrafiltration membrane, silica, rejection

1. Introduction

Cross-flow ultrafiltration is now used in a wide range of industrial applications in the food industry, in biotechnology, in the pharmaceutical industry, and in water and wastewater treatment. The nominal molecular-weight cut-off for ultrafiltration membranes is around 1-300 kDa. Ultrafiltration membranes primarily filter molecules, and they can be evaluated by determining the membrane performance cut-off with molecular weight.

Recently, inorganic nanoparticles have attracted attention, because of their specific properties due to quantum effects. Because the interesting properties of nanoparticles are strongly related to particle size, size-controlling techniques that can achieve a narrow pore size distribution are important. The size of nanoparticles is of a similar magnitude to that of molecules separated by ultrafiltration membranes, and therefore ultrafiltration membranes can be used to separate nanoparticles. The

transport mechanism of molecules in ultrafiltration membranes has been deduced[1,2], but there have been few studies on separating inorganic nanoparticles using ultrafiltration membranes. Assuming that a membrane rejects nanoparticles completely, Zhang et al[3-5]. and Bacchin et al[6]. developed a model for the permeate flux in cross-flow ultrafiltration. However, no studies on particle size separation using an ultrafiltration membrane have been reported. To achieve the separation of nanoparticles using ultrafiltration membranes, it is necessary to evaluate the rejection properties of nanoparticles having similar, or smaller particle diameters than the pore sizes of a membrane.

The purpose of this study was to clarify the rejection properties of nanoparticles in ultrafiltration membranes using cross-flow permeation experiments. We used silica nanoparticles and polycarbonate track-etch flat membranes because the particle size distribution of the silica nanoparticles and the pore size distribution of the membranes were very narrow. The relationship between these two variables was assessed by changing the

[†] Author for all correspondences
(e-mail : takaba@chemsys.t.u-tokyo.ac.jp)

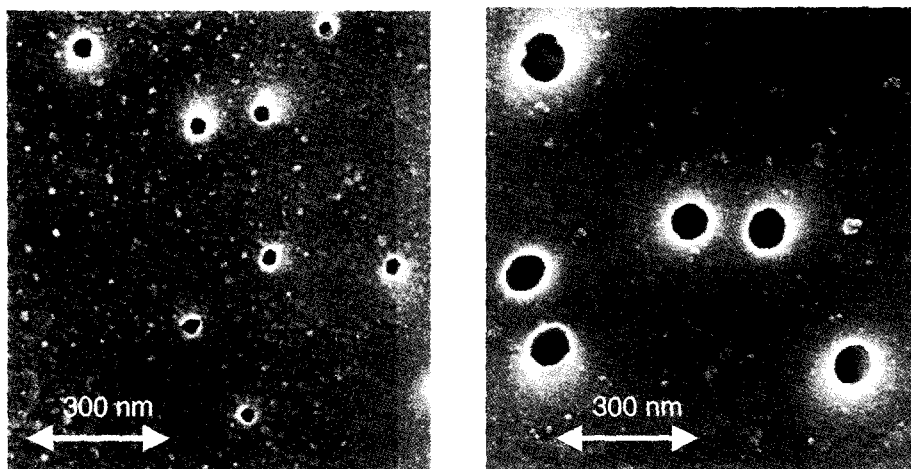


Fig. 1. SEM images of polycarbonate track-etch membranes with pore sizes of 30 nm (left-hand side) and 50 nm (right-hand side).

experimental parameters. In this study, the operating parameters used were feed concentration, pH, and ionic strength. Similar permeation experiments were also conducted using dextran, which has almost the same particle size as the silica nanoparticles, to investigate the influence of inherent particle size.

2. Experimental

Silica nanoparticles from Shokubai Kasei Kogyo, Inc., Tokyo, Japan were selected as the model inorganic nanoparticles for the filtration experiments. Two types of silica nanoparticles were used, having mean diameters of 5 and 18 nm with narrow particle size distributions. Two types of dextran with molecular weights of 70,000 and 150,000 were used to compare the results obtained using the silica nanoparticles with those obtained using another molecular polymer. The mean particle diameters of the dextran used were 8 nm (Pharmacia, Ficoll 70, Sweden) and 15 nm (M.W. = 200 000~300 000, Wako Inc., Japan).

Polycarbonate track-etch flat membrane from Osmonic Inc., U.S.A., was selected as the ultrafiltration membrane. The membrane characteristics included a narrow pore size distribution arising from its unique preparation method[7]. The mean pore diameters were 30 and 50 nm. Scanning electron microscope (SEM, S-900, Hitachi, Japan) images of these membranes are shown in Figure 1.

Ultrafiltration experiments were carried out using the apparatus shown in Figure 2. The module used was a thin-channel flow cell supplied by Nittq-Denko, Japan. The effective membrane width was 46 mm, and the membrane was 180 mm in length. The channel height of the cell was 0.85 mm. The standard conditions for ultrafiltration were conducted using a feed flow rate of 1.0 l/min and a feed temperature of 20°C. A new membrane was used for each permeation experiment, and the membrane performance was checked by measuring the flux of pure water. The permeate was collected in a beaker and weighed using an electronic balance. The silica nanoparticle concentration in the feed solution and the permeate was measured using gel permeation chromatography (GPC, HLC-8220GPC, Tosoh Inc., Japan). Sadasivan et al[8], and Ono[9] reported that GPC measurements are an effective method to measure the size distribution of silica nanoparticles. By using GPC, it was confirmed that no aggregation of silica nanoparticles occurred in any of the experiments. The dextran concentration was measured using a total organic analyzer (TOC, TOC-5000, Shimadzu Inc., Japan).

3. Results and Discussion

3.1. Rejection Factors of the Silica Nanoparticles and Dextran

Ultrafiltration experiments were conducted using silica

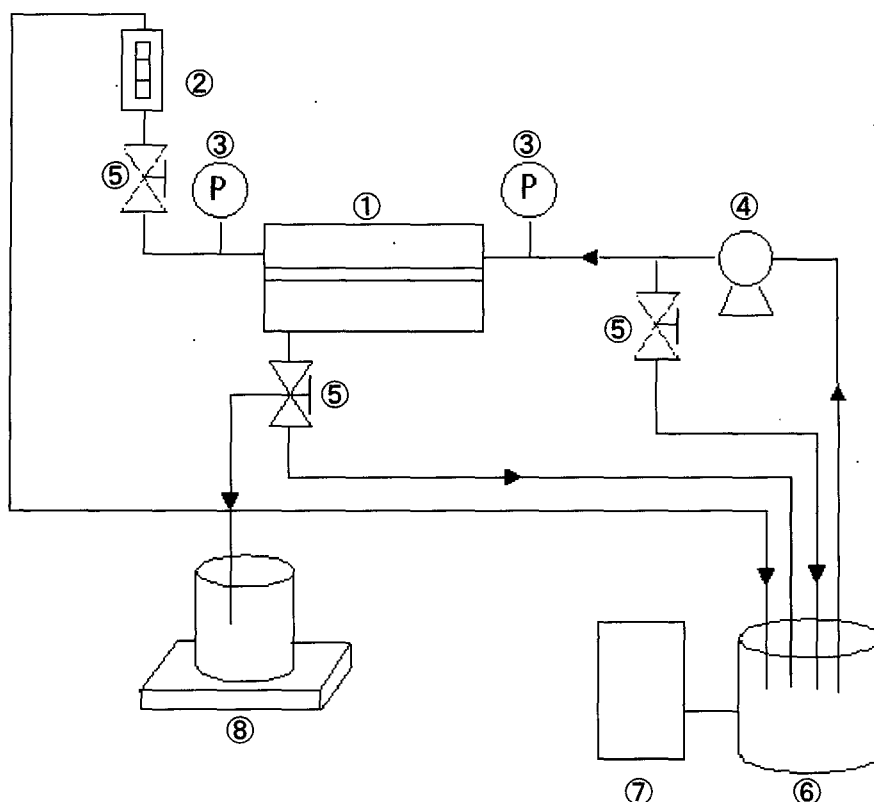


Fig. 2. A schematic drawing of the apparatus used in the ultrafiltration experiments. Key: 1 = membrane module; 2 = flow meter; 3 = pressure gauge; 4 = pump; 5 = valve; 6 = feed tank; 7 = thermostat; and 8 = balance.

Table 1. The results of ultrafiltration experiments using silica nanoparticles. Key: d_s = particle diameter; C_0 = feed concentration; d_p = pore diameter; ΔP = applied pressure; J_{v-R} = pure water flux; J_{v-S} = solution flux; and R_{obs} = observed rejection factor

d_s (nm)	C_0 (ppm)	d_p (nm)	ΔP (kPa)	J_{v-R} ($\text{m}^3/\text{m}^2 \cdot \text{s}$)	J_{v-S} ($\text{m}^3/\text{m}^2 \cdot \text{s}$)	J_{v-S}/J_{v-R}	R_{obs} (%)
5	1.5×10^3	30	97.5	2.12×10^{-5}	2.01×10^{-5}	0.948	>99
5	9.2×10^2	50	31	3.39×10^{-5}	2.81×10^{-5}	0.829	>99
18	1.2×10^2	30	92.2	2.95×10^{-5}	2.60×10^{-5}	0.881	>99

Table 2. The results of ultrafiltration experiments using dextran. Key: d_s = particle diameter; C_0 = feed concentration; d_p = pore diameter; ΔP = applied pressure; J_{v-R} = pure water flux; J_{v-S} = solution flux; and R_{obs} = observed rejection factor

d_s (nm)	C_0 (ppm)	d_p (nm)	ΔP (kPa)	J_{v-R} ($\text{m}^3/\text{m}^2 \cdot \text{s}$)	J_{v-S} ($\text{m}^3/\text{m}^2 \cdot \text{s}$)	J_{v-S}/J_{v-R}	R_{obs} (%)
8.06	92.54	10	68.2	4.80×10^{-7}	6.15×10^{-7}	0.780	21.3
8.06	87.86	30	75.5	3.12×10^{-5}	2.89×10^{-5}	0.926	3.62
15.00	95.45	30	74	2.86×10^{-5}	1.96×10^{-5}	0.685	4.38

nanoparticles as the solute with particle diameters smaller than the pore size of the membrane. The results are summarized in Table 1, which shows that the membranes rejected almost all the particles, even when the particle size was much smaller than the pore diameter

of the membrane. Table 2 shows the results of ultrafiltration experiments using dextran as the solute. The dextran solute used had almost the same particle size as the silica particles. Despite the similar particle size between dextran and silica, a lower rejection was

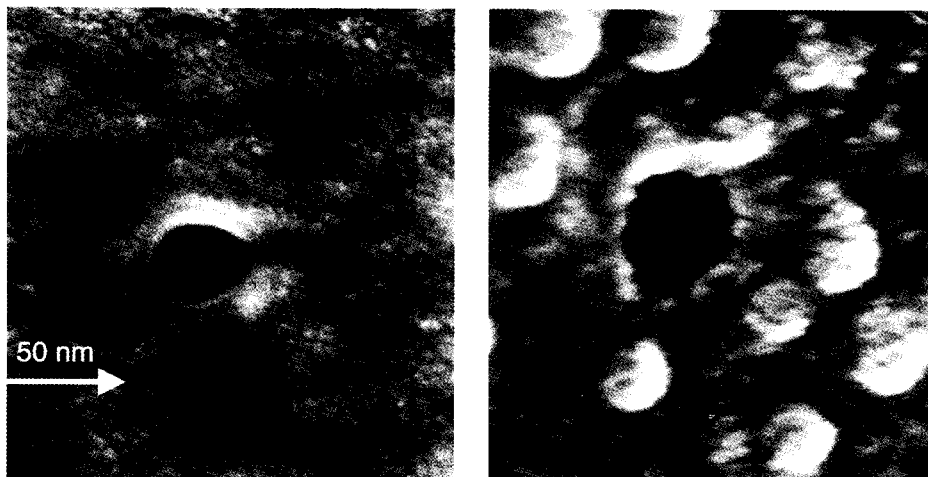


Fig. 3. SEM images of a membrane with pore size = 30 nm before (left-hand side) and after (right-hand side) the experiment.

observed for dextran.

These results suggest that there are different transport mechanisms between the silica nanoparticles and dextran. SEM images of the membrane before, and after ultrafiltration experiments conducted with 18 nm-diameter particles using a membrane having a pore diameter of 30 nm are shown in Figure 3. As can be seen in Figure 3, no particles were observed inside the pores. Sonnefeld[10] et al. and Sotozaki[11] each reported both polycarbonate membranes and silica nanoparticle have negative charges on their surface. Hence, we suppose that the reason for the higher observed rejection for silica nanoparticles is due to electrostatic repulsion between the particles and the membrane.

3.2. Effect of the Ionic Strength of the Solution

To confirm the effect of electrostatic repulsion on the rejection rate, ultrafiltration experiments using silica nanoparticles were carried out using solutions to which various concentrations of KCl were added to change the ion strength. The experimental conditions of low flux and low KCl concentration were selected to obtain a steady state. The conditions for the ultrafiltration experiments were: particle diameter = 5 nm; particle concentration = 200 ppm; pore diameter = 50 nm; and applied pressure = 8.0 ± 0.5 kPa. Using these experimental conditions, the flux of pure water was $2.0 \pm 0.3 \times 10^{-5}$ m³/m²s. The change in permeate fluxes and

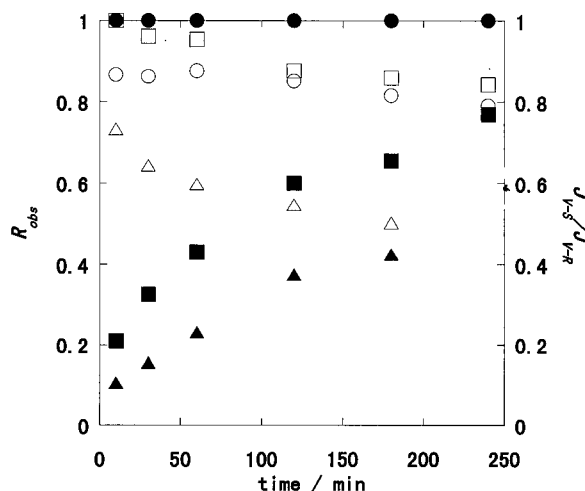


Fig. 4. The dependency of permeate flux and rejection factor on KCl concentration. Key: O and ● = [KCl] = 0 mM; □ and ■ = [KCl] = 3 mM; and △ and ▲ = [KCl] = 10 mM.

the observed rejection, R_{obs} , with time are shown in Figure 4. The R_{obs} and flux decreased with increasing KCl concentration. On adding KCl the electrostatic repulsion is reduced, and this enables the silica nanoparticle to enter into and pass through the pores. As time proceeds, the flux decreases and the rejection increases. Under our experimental conditions, the steady state could not be achieved.

3.3. Effect of the pH of the Solution

The ultrafiltration experiments described in the previous

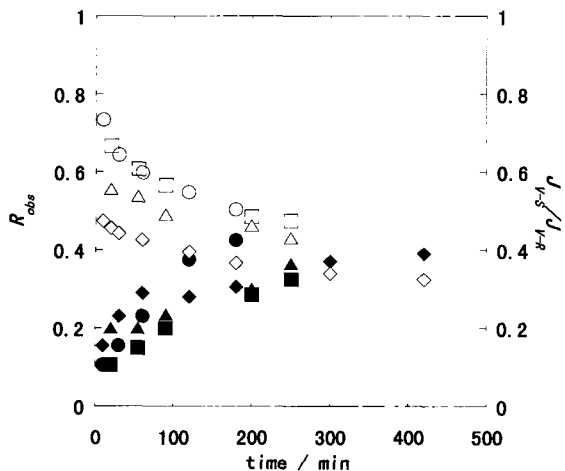


Fig. 5. The dependency of the permeate flux and rejection factor on pH. Key: O and ● = (pH = 9.2); □ and ■ = (pH = 8.4); and △ and ▲ = (pH = 7.4).

section were carried out using solutions with pH = 10. The isoelectric point of silica particles is about 2.4, and thus the surface charge density of silica nanoparticles in the above experiments would have been relatively large[10]. Ultrafiltration experiments using solutions with lower pH values were therefore carried out. HCl and NaOH solutions were used to adjust the pH. The experimental conditions used for the ultrafiltration experiments were: particle diameter = 5 nm; particle concentration = 200 ppm; pore diameter = 50 nm; applied pressure = 8.0×0.7 kPa; and KCl concentration = 10 ± 1 mM. Under these conditions, the flux of pure water was $2.0 \pm 0.3 \times 10^{-5}$ m³/m²s. The change in permeate flux and the R_{obs} with time are shown in Figure 5. As the pH decreased, both the permeate flux and the rejection decreased, although the change in R_{obs} was not very apparent. In the solution with pH = 6.5, the permeate flux and R_{obs} approach the steady state faster than for other solutions with different pHs. From these results, a decrease in pH significantly increases R_{obs} , and this would be due to the decrease in surface charge of the particles. This supports the idea that the electrostatic repulsion is the main reason for the high rejection rates in this system.

3.4. Steady State Experiments

The achievement of the steady state in which the

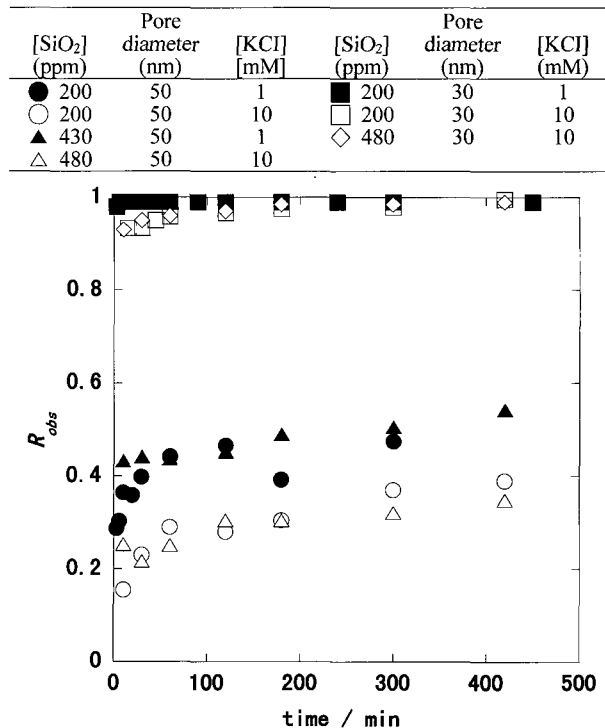


Fig. 6. The dependency of the rejection factor on various operating parameters when the pH of the solution was pH = 6.5.

flux and low rejection factor remain constant for a long time is important in the practical separation of nanoparticles. In the previous sections, it was shown that the steady state was observed when the pH of the solution was pH = 6.5. Therefore, the membrane performance using a solution with pH = 6.5 under various experimental conditions was investigated further. The experimental conditions used were: particle diameter = 5 nm; pore diameter = 30 or 50 nm; and applied pressure = 52 ± 2 kPa when the pore size = 30 nm, and 8.0 ± 0.5 kPa when the pore size = 50 nm. Under these conditions, the flux of pure water was $2.0 \pm 0.1 \times 10^{-5}$ m³/m²s and $2.0 \pm 0.1 \times 10^{-5}$ m³/m²s for pore sizes of 30 and 50 nm, respectively.

The conditions used in the experiments, and the results from the change in permeate flux and R_{obs} as a function of time are shown in Figures 6 and 7. Under these conditions, the steady state was obtained after 60 min. In the particle concentration range of a few hundreds of ppm, no dependency of the permeate flux

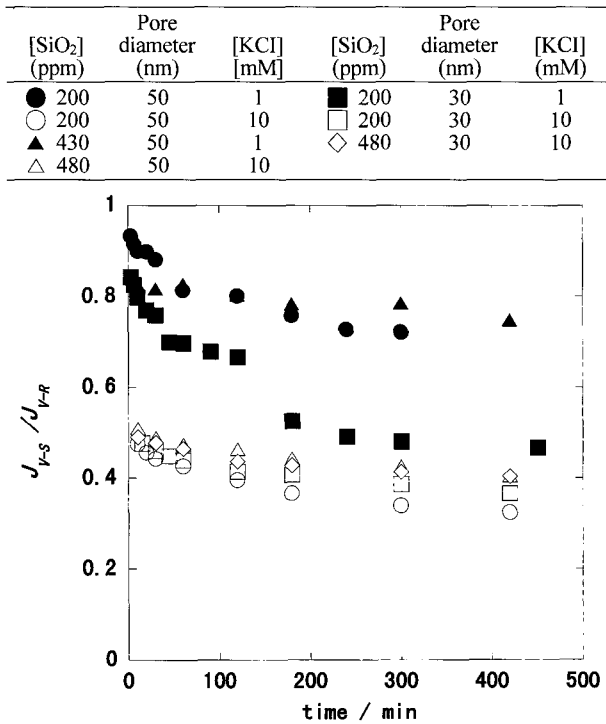


Fig. 7. The dependency of the flux on the various operating parameters when the pH of the solution was pH = 6.5.

on the feed concentration was observed. The R_{obs} were around 30-40% for the membrane with a pore size = 50 nm, and the R_{obs} was almost 1.0 for the membrane with a pore size = 30 nm. However, It can be seen that the permeate flux and the R_{obs} were dependent on the KCl concentration.

It is difficult to understand why the particles were rejected by the membrane having a much larger pore size than that of particles, even when the repulsion interaction between the particles and membranes was supposed to be insignificant. One possible reason is the retention of the particles by the pores. SEM images taken before and after the experiments are shown in Figure 8 (the experimental conditions were: pore diameter = 50 nm, and [KCl] = 10 mM). Many particles were observed at the membrane surface, and some of the pores were difficult to distinguish from the surface region, because the pore had been plugged by the particles. It is supposed that pore blockage is the main reason for the high rejection rates for these membranes.

4. Conclusions

The rejection properties of silica nanoparticles differed greatly to those of dextran. Ultrafiltration membranes showed higher rejection factors than expected because of a molecular cut-off by the membranes. By changing the pH to 6.5, steady state flux conditions could be obtained.

We have shown that the permeate flux and rejection factors are highly dependent on ionic strength and pH. This result suggests that the surface charges of the silica nanoparticles and their electrostatic interaction

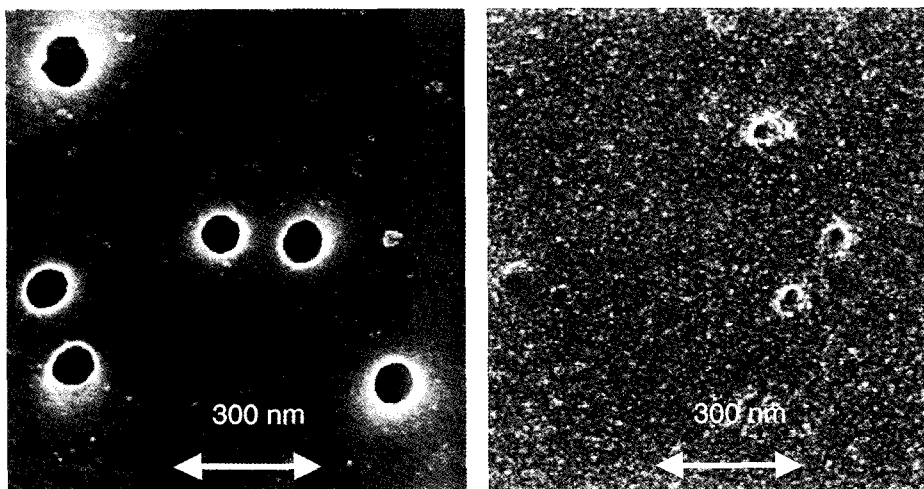


Fig. 8. SEM images of the membrane before (left-hand side), and after (right-hand side) the experiment.

with the membranes significantly influences the rejection properties of silica nanoparticles.

The rejection properties of silica nanoparticles cannot be explained by conventional permeation theory based on a size exclusion effect. Therefore, further theoretical investigation is required using similar treatments as used in nanofiltration to explain these transport phenomena.

References

1. S. Nakao and S. Kimura, *J. Chem. Eng. Japan*, **14**, 32 (1981).
2. S. Nakao and S. Kimura, *J. Chem. Eng. Japan*, **15**, 200 (1982).
3. L. Song and M. Elimelech, *J. Chem. Soc. Faraday Trans.*, **91**, 3389 (1995).
4. L. Song, *J. Colloid Interface Sci.*, **214**, 251 (1999).
5. M. Zhang and L. Song, *J. Environ. Eng.* **126**, 667 (2000).
6. P. Bacchin, D. Si-Hassen, V. Starov, M. J. Clifton, and P. Aimar, *Chem. Eng. Sci.*, **57**, 77 (2002).
7. M. Cheryan, PhD thesis, "Ultrafiltration Handbook", Technomic Publishing Company
8. S. Sadasivan, D. H. Rasmussen, F. P. Chen, and R. K. Kannabiran, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **132**, 45 (1998).
9. S. Ono, *Koubunshi Ronbunshu*, **49**, 759 (1992).
10. J. Sonnefeld, M. Lobbus, and W. Vogelsberger, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **195**, 215 (2001).
11. T. Sotozaki, *MSc thesis*, University of Tokyo, Japan, (Japanese) (1996).