

Development of Transport Parameters affecting on the Removal of Micro Organic Compounds such as Disinfection By-Products and Pharmaceutically Active Compounds by Low-Pressure Nanofiltration

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Abstract

This study investigated the removal characteristics of various micro organic compounds by low-pressure nanofiltration membranes comprised of disinfection by products and pharmaceutically active compounds. The experimental removal of micro organic compounds by low-pressure nanofiltration membranes was compared with the transport model calculations, which consist of diffusion and convection terms including steric hindrance factor. The selected molecule from the disinfection byproducts and pharmaceutical active compounds showed a much lower removal than polysaccharides with a similar molecular size. However, the difference between model calculation and experimental removal of disinfection by-products and pharmaceutically active compounds could be corrected. The correlation of K_s with solute radius was further considered to clarify transport phenomena of micro organic solutes through nanofiltration membranes.

Keywords: Nanofiltration, Steric hindrance, Disinfection byproducts, Pharmaceutical active compounds

1. Introduction

Membrane processes are generally divided into microfiltration (MF), ultrafiltration (UF), and reverse osmosis (RO), which employ pressure differentials. Nanofiltration has intermediate characteristics between reverse osmosis and ultrafiltration, and has been used in several areas including water softening, treatment of heavy metals contained in industrial wastewater, removal of trace chemical substances e.g., natural organic matters, precursors for trihalomethane formation, inorganic salts in river water etc.¹⁻⁷⁾ In particular, low-pressure nanofiltration is attractive for treating fresh water, because fresh water has much lower osmotic pressure than seawater where a desalination technology such as reverse osmosis has been applied.^{8,9)} The separation characteristics of nanofiltration depend on the molecular charge as well as molecular size of target solutes because nanofiltration membranes become negatively or positively charged ones in neutral pH condition. While removal of ions is due to size exclusion and charge effect, removal of neutral-charge compounds is

closely related to size exclusion during nanofiltration.

However, the characteristics of nanofiltration membrane separation has been evaluated by nominal salt removal and molecular weight cutoff size, although these conventional indicators are not enough to explain the removal characteristics of various trace inorganic/organic pollutants by nanofiltration. When trace neutral organic solutes, which have smaller molecular weight than molecular weight cutoff of membranes, flow through membrane, what kind of interaction can be affected on the removal characteristics was not clearly explained. It might come to draw direction of membrane development such as selectivity of materials, coating technique and so on. With this view, it is important to investigate transport phenomena of solutes through nanofiltration membranes.

Recently, the removal of micro organic compounds such as endocrine disrupters, plasticizer, and volatile organic compounds, pharmaceutically active compounds and disinfect by products are interested in water and wastewater treatment process, because the demand of high quality water supply is continually increased.¹⁰⁻¹³⁾ These materials exist in water at low concentration although they have high toxicity for human health. Considering applicability of low-pressure nanofiltration to drinking water treatment plant, the removal phenomena of micro-organic com-

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pounds in low operational pressure range must be important to suggest the appropriate design of nanofiltration plants. With this view, this study aims to investigate transport factors of micro organic compounds such as disinfection by products, pharmaceutically active compounds, of which character was trace neutral solutes, through nanofiltration membranes and to develop appropriate transport models of nanofiltration, considering mutual interaction between membranes and solutes.

2. Material and Methods

2.1. Nanofiltration

Nanofiltration experiments were conducted by using a cross flow nanofiltration unit as shown in Fig. 2. A membrane module is a flat sheet type with an effective surface area of 60 cm².

Filtration experiment was basically conducted for one set of each solution condition such as operational pressure. For each experiment of nanofiltration, operation time is approximately 6 hours. Bulk and permeate solution is collected as sample at each 2 hours. Generally samples were taken after 2 hours from the introduction of the feed solution to enable steady state conditions of permeate membrane surface were thus eliminated. Consequently, 3 samples are obtained from both bulk and permeate for each experiment. The removal of a compound *i*, R_i (%), was calculated using the expression of $R_i = (1 - C_{p,i} / C_{r,i}) \times 100(\%)$. Where $C_{p,i}$ and $C_{r,i}$ are the concentration for permeate and retentive. Removal values were measured at low membrane pressures under 0.5MPa. Nanofiltration membrane used was negatively charged membrane and made of polyvinyl alcohol/polyamide. Nominal salt removal of nanofiltration membrane used was 93%.

Target solutes were pointed out to be polysaccharides (Maltose (Mal), Glucose (Glu), 1-Propanol (Pro), Ethanol (Eth)), disinfection by products (Dibromochloromethane (DBCM), Bromodichloromethane (BDM), Chloroform (Chlo), Bromoform (Brom)) and pharmaceutical active compounds (Phenacetine (Phena), Primidone (Primi)), of which molecular weight is below 500 Daltons. Removal of the target solutes by low-pressure nanofiltration was examined with a different operational pressure at 0.25, 0.4 and 0.5 MPa, where the permeate flux and circulating flow for each operational condition was shown in Table 1. The operational pressure range of nanofiltration was installed under 0.5MPa, because this study aimed to clarify the transport phenomena of micro organic compounds such as disinfection by-products, and pharmaceutically active compounds by low pressure nanofiltration in drinking water production. Moreover, the experimental removal of target solutes in mixed solution under low pressure operational range of nanofiltration was similar with their each removal in single solution by nanofiltration. Considering applicability of low-pressure nanofiltration to drinking water treatment plant, the removal phenomena of micro-organic compounds in low operational pressure range must be important to suggest the appropriate design of nanofiltration plants. With this view, the mixed standard solution was utilized in the experiment of nanofiltration to investigate removal characteristics of

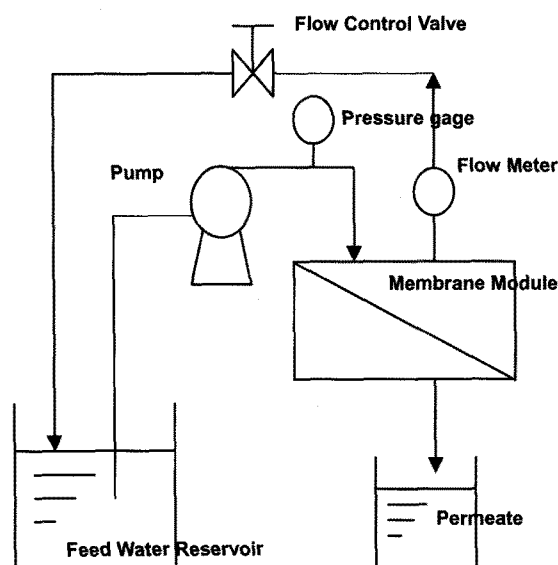


Fig. 1. Schematic diagram of cross-flow nanofiltration experimental set-up.

Table 1. Nanofiltration membrane used and operational condition

	Nanofiltration membranes		
Operational pressure (MPa)	0.25	0.4	0.5
Permeate flux (m ³ /m ² /day)	0.16	0.27	0.35
Circulating flow(L/min)	1.8	1.8	1.8
Temperature(°C)	25	25	25

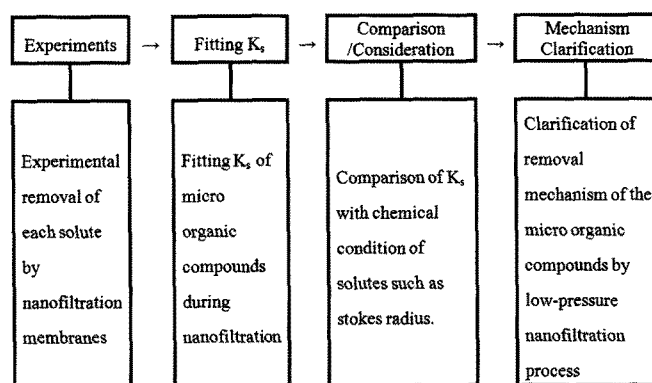


Fig. 2. Flow diagram of evaluation methods of removal characteristics of micro organic compounds by low-pressure nanofiltration membranes.

micro-organic compounds such as disinfection by-products, and pharmaceutically active compounds. The schematic diagram of cross-flow nanofiltration experimental set-up was shown in Fig. 1.

The tap water, to which 1mg/L of polysaccharides, disinfection by products and pharmaceutical active compounds with 5% leachate of constituted volume were added, utilized the synthetic feed water. In the case of disinfection by products and pharmaceutical active compounds, the mixed standard solution was prepared by dissolving these compounds in acetone. The reason why feed solution of nanofiltration membrane was prepared by dissolving target compounds in acetone was that consideration of chemical existence for target solutes in water. The micro-organic compound dissolved in acetone would be similar with

their chemical existence in water, comparing with them dissolved in methanol or other solvent. On the other hands, the addition reason for the leachate, which was taken from a municipal landfill site for solid waste disposal and filtered to be suspended solid free, was to reduce adsorption of the target solutes. The "5% leachate of constituted volume in feed water for nanofiltration experiments were also considered the chemical existence for target solute in real water environments such as river water, groundwater in which abundant humic acid were existed. The transport phenomena of micro organic compounds such as disinfection by-products and pharmaceutically active compounds in nanofiltration were not clearly clarified in the real water environments (for example, surface water).

2.2. Chemicals

Main target materials by nanofiltration membrane are pointed out to be polysaccharides, disinfection-by products and pharmaceutical active compounds of which molecular weight is below 500 Daltons. Chemical reagents used are listed in Table 2. The pH of synthetic feed solution was adjusted at 7~8 by using sodium hydroxide and hydrate chloride.

Polysaccharides and pharmaceutical active compounds were measured by the liquid chromatograph (LC-10AD, Shimadzu Corporation) methods. Disinfection-by-products such as Dibromochloromethane (DBCM), Bromodichloromethane (BDM), Chloroform (Chlo), Bromoform (Brom) were analyzed by using Gas chromatography/Mass spectrometer (GC/MS, Shimadzu Corporation GC-17A, QP5000A). Before the injection into the port of GC/MS used with the selected ion monitoring (SIM) quantification, the disinfection by products were extracted by using the solid phase micro extraction (SPME, Spec Co. Ltd.) methods. The solid phase micro extraction fiber, the target samples were absorbed, was injected into GC/MS with quantification of the target samples in the SPME with GC/MS.

3. Results and Discussion

3.1. Theoretical Consideration

The model methodology was considered under the condition of mixed solution, and was utilized to predict the performance

of nanofiltration for trace neutral molecules, which have different molecular weight.

As shown in Eq. (1), the transport equation of solutes through nanofiltration membranes consists of diffusion and convection term coupled with correction factors.

$$j_v = -K_D D_s \frac{dc_s}{dx} + K_F c_s J_v \quad (1)$$

$$K_D = (1 - r_s/r_p)^2 \quad (2)$$

$$K_F = (1 + 16/9(r_s/r_p)^2) (1 - (r_s/r_p)^2) (2 - (1 - (r_s/r_p)^2)^2) \quad (3)$$

In conventional model, a transport equation is modified by two parameters of K_D and K_F , which is correction of diffusion and convection term.¹⁴⁾

The steric hindrance factors of K_D and K_F in the transport equation depend on the ratio of permeable solute radius to pore radius of membranes as shown in Eq. (2) and Eq. (3). At this point, another factor except steric hindrance effect was assumed to be affected on separation characteristics of nanofiltration, depending on chemical condition of solutes such as solubility, molecular structure and so on.

With this view, Fig. 1 represents the flow diagram of evaluation methods for removal characteristics of micro organic compounds by low-pressure nanofiltration membranes. There were four steps to evaluate removal characteristics of micro-organic compounds such as disinfection by-products, pharmaceutical active compounds and polysaccharides. First, removal of each target solute by nanofiltration membranes was investigated. Second, the factor except steric hindrance effects for each target solutes during nanofiltration was fitted with experimental removal. Third, the role of the factor except steric hindrance effect for each target solutes obtained from fitting with experimental removal were considered by comparing with chemical condition of solutes such as solubility, molecular structure, polarity and so on. Finally, removal characteristics of the micro organic compounds such as disinfection by-products, pharmaceutical active compounds and polysaccharide by low-pressure nanofiltration process would be clarified and the factors affecting on removal of micro organic compounds such as disinfection by-

Table 2. Physical properties of the target solutes

Target Solutes	Abbrev.	M.W.	Chemical Formula	
Disinfection by products	Dibromochloromethane	DBCM	208	CHBr ₂ Cl
	Bromodichloromethane	BDM	164	CHBrCl ₂
	Chloroform	Chlo	119	CHCl ₃
	Bromoform	Brom	253	CHBr ₃
Pharmaceutucial active compounds	Phenacetine	Phena	179	C ₁₀ H ₁₃ NO ₂
	Primidone	Primi	218	C ₁₂ H ₁₄ N ₂ O ₂
Polysaccharides	Maltose	Mal	342	C ₁₂ H ₂₂ O ₁₁
	Glucose	Glu	180	C ₆ H ₁₂ O ₆
	1-Propanol	Pro	60	C ₃ H ₈ O
	Ethanol	Eth	46	C ₂ H ₆ O

products and pharmaceutically active compounds by low-pressure nanofiltration would be also founded.

3.2. Correction Factors for Diffusion and Convection

The experimental removal of disinfection by-products and pharmaceutical active compounds could not be well described by model calculation. Another factor except steric hindrance effect was necessary to explain the removal characteristics of micro-organic compounds such as disinfection by-products and pharmaceutical active compounds.

At this point, the factor of K_s was introduced to the transport equation to describe mutual interaction between membrane and micro organic compounds. At low pressure of nanofiltration, the range of volume flux change is not so large. Therefore, the interaction factor of K_s at low-pressure nanofiltration was applied to both diffusion and convection term in the transport equation. The K_s is unknown parameter and fitted with experimental removal of each target micro organic pollutants by low-pressure nanofiltration membranes.

The diffusion term is independent of pressure, the convection term is proportional to the pressure because of Hagen-Poiseuille's law. In the hypothetical case of an infinite pressure, diffusion is negligible compared to the infinite convection flux. Since diffusion of solutes results in an increase of transport relative to the water transport, the relative transport of solutes is the lowest at infinite pressure.¹⁵⁾

At low pressure of nanofiltration, operational pressure range is not so large so that volume flux is not so different. Therefore, both diffusion and convection terms contribute to the transport of solutes through the membrane. The correction parameter of K_D and K_F at low-pressure nanofiltration may be similar effect for both terms under low pressure nanofiltration.

Considering applicability of low-pressure nanofiltration to drinking water treatment plant, the removal phenomena of micro-organic compounds in low operational pressure range must be important to suggest the appropriate design of nanofiltration plants. In the case of low pressure operational range for nanofiltration, the factor of K_D and K_F were affected on the transport phenomena of micro organic compounds during nanofiltration. That is to say, the simplified type of correction factor K_s could be suggested in the case of low-pressure nanofiltration.

Almost correction factors of diffusion and convection terms in the transport equation are described by steric hindrance effects, which depend on the ratio of permeable solute radius to pore radius of membranes. However, considering real surface structure of nanofiltration membranes, pore size is not so different from solute size with the scale of nanofiltration and the pores are not straight and cylindrical but are irregular and various size. Hence, the equations for conventional steric hindrance factor in nanofiltration membrane pores may have limitation to describe actual porous membrane.

With this view, the correction parameter of K_D and K_F at low pressure nanofiltration was suggested to be simplified here in this study. The simplified type of correction factor, K_s , was introduced in the transport equation as shown in Eq. (4).

$$j_s = -K_s D_s \frac{dc_s}{dx} + K_s c_s J_V \quad (4)$$

It is based on the assumption that pore is represented by porosity although pore is existed in membrane. When a solute is diffusing through membrane having various sizes of pores, a solute will be collided to the wall during filtration. At that time, larger size of solute has more collision or friction to membrane wall so that removal is corresponding to size of solute. The K_s is represented by a function of solute radius. It is unknown parameter.

The removal phenomena of micro-organic compounds in low operational pressure range must be important to suggest the appropriate design of nanofiltration plants, considering applicability of low-pressure nanofiltration to drinking water treatment plant. In the case of low pressure operational range for nanofiltration, the factor of K_D and K_F were affected on the transport phenomena of micro organic compounds during nanofiltration. That is to say, the united type of correction factor K_s could be suggested in the case of low-pressure nanofiltration. In this study, the K_s included both steric-hindrance and interaction factors between membrane and target solutes. Especially, we assumed that the K_s of polysaccharides such as maltose, glucose, 1-propanol and ethanol were 1 in the case of K_s factor comparison, because there were no interaction between membrane material and polysaccharides because of no experimental adsorption to membrane polymer during nanofiltration experiments. On the other hands, the K_s of target solute was not 1, the solute was assumed to represent some kind of interaction with membrane materials.


There are one unknown parameter in model calculation; correction factor for diffusion and convection term (K_s). It was obtained from the curve fitting of the experimental removal of sugars and alcohols with calculation of model. From the simulation of removal of disinfection by-products and pharmaceutical active compounds, each K_s of solutes could be obtained as shown in Table 3.

3.3. Numerical Model Calculation


The flow diagram of calculation was shown in Fig. 3. This diagram shows how to calculate permeate concentrations by the model proposed here. Permeate concentrations were properly assumed before step-by-step calculation in filtration direction. The concentrations inside membrane at the bulk side edge were calculated from bulk concentrations. A set of transport equation coupled with simplified correction factor was used to calculate the concentration profiles inside the membrane. This calculation procedure was repeated until that the calculated permeate concentration approaches the given permeate concentration. There is one unknown parameter in model calculation: interaction factor (K_s). It was obtained from the curve fitting of the experimental removal of solutes with calculation of model. At this point, the general membrane parameter of pore radius and porosity in the case of steric hindrance pore model was further included in the factor K_s of target solutes. That is to say, this model methodology was simplified.

Table 3. Obtained K_s for micro-organic compounds by nanofiltration and molecular structure of pharmaceutical active compounds and disinfection by-products


Target Solutes	Abbrev.	M.W.	$K_s(-)$
Dibromochloromethane	DBCM	208	85.0
Bromodichloromethane	BDM	164	7.70
Chloroform	Chlo	119	2.92
Bromoform	Brom	253	1250
Phenacetine	Phena	179	15.8
Primidone	Primi	218	117
Maltose	Mal	342	1.0
Glucose	Glu	180	1.0
1-Propanol	Pro	60	1.0
Ethanol	Eth	46	1.0




Dibromochlorometh



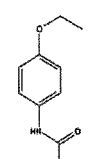
Bromodichlorometha



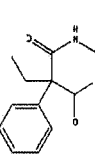
Chloroform



Bromoform



Phenacetin



Primidone

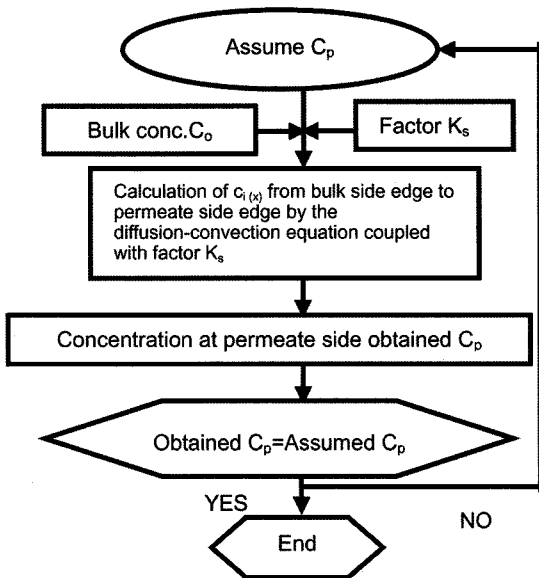


Fig. 3. Flow diagram of numerical calculation for the Diffusion-Convection transport model considering factor K_s .

At this point, we assumed that the K_s of polysaccharides such as maltose, glucose, 1-propanol and ethanol were 1. That is to say, there were no interaction between membrane material and polysaccharides because of no experimental adsorption to membrane polymer during nanofiltration experiments. The K_s of target solute was 1, the solute was assumed to represent no interaction with membrane materials.

3.4. Experimental Removal

Removal characteristics of polysaccharides, disinfection by products and pharmaceutical active compounds by nanofiltration membrane with different operational pressures under 0.5MPa were investigated. The maximum permeate flux of nanofiltration under low pressure range was exhibited by $0.35 \text{ m}^3/\text{m}^2/\text{day}$. Although the membrane experiments were conducted by using mixed synthetic feed solution to which target solutes such as polysaccharides, disinfection by products and pharmaceutical active compounds were added at the same time, the removal characteristics of target solutes by nanofiltration membrane were described by Fig. 4, Fig. 5 and Fig. 6 separately.

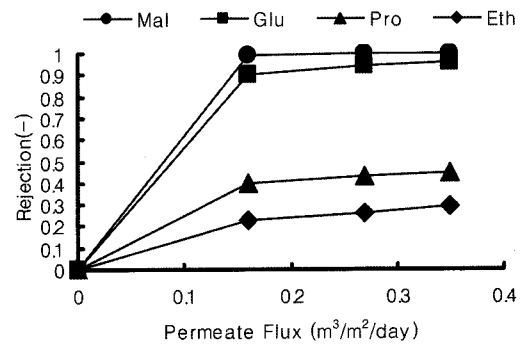


Fig. 4. Rejection characteristics of polysaccharides such as maltose, glucose, propanol and ethanol with different operation pressure under 0.5MPa at nanofiltration.

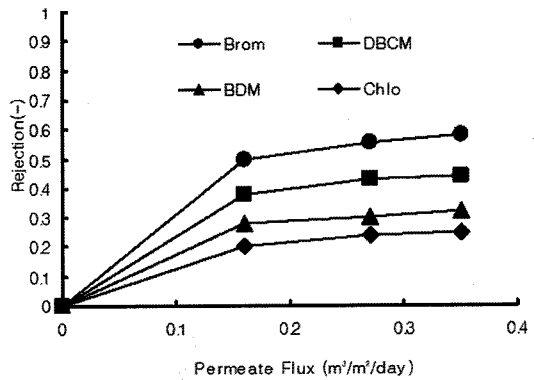


Fig. 5. Rejection characteristics of disinfection by products such as bromoform, dibromochloromethane, bromodichloromethane and chloroform with different operation pressure under 0.5MPa at nanofiltration.

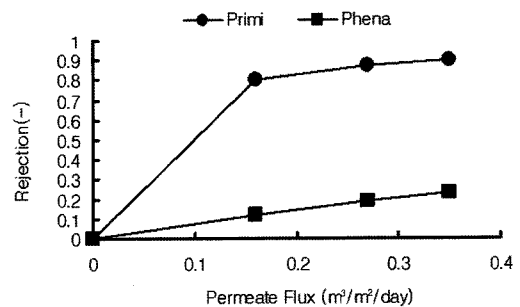


Fig. 6. Rejection characteristics of pharmaceutical active compounds such as primidone and phenacetin with different operation pressure under 0.5MPa at nanofiltration.

As the removal of solutes by nanofiltration membranes were increased with the permeate flux, the removal difference between the permeate flux of $0.16 \text{ m}^3/\text{m}^2/\text{day}$ and $0.35 \text{ m}^3/\text{m}^2/\text{day}$ for every target solute were under 10% approximately. With this view, the operational range of this experiment would not affect the removal rate of micro-organic compounds such as polysaccharide, disinfection by-products and pharmaceutical active compounds.

3.5. Comparison of Experimental Removal with Model Calculation

Comparison of experimental removal with the model calculation on the basis of stokes radius of target solutes without considering factor K_s was shown in Fig. 7. The polysaccharides used were maltose, glucose, 1-propanol and ethanol. They normally consist of carbon, hydroxide and oxygen and exist in non-charge solute as shown in Fig. 8. In general, removal characteristics of non-charged solutes can be explained by sieving effect. Therefore, charge effect of nanofiltration membranes is negligible in the case of non-charged solutes. Sugars and alcohols are thought

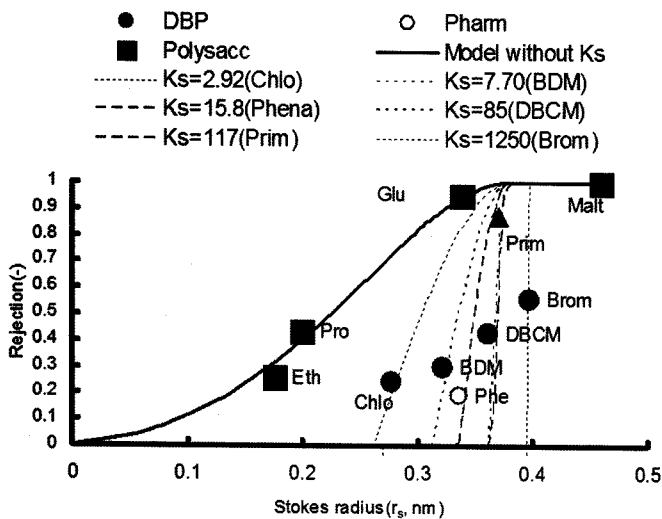


Fig. 7. Comparison of experimental rejection of disinfection by-products (DBP), pharmaceutical active compounds (Pharm) and polysaccharides with model calculation, no consideration of K_s .

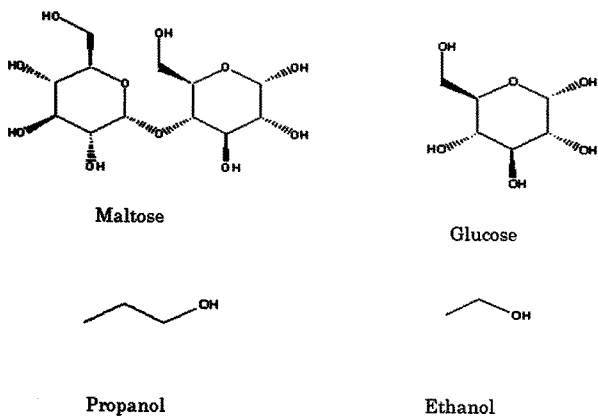


Fig. 8. Molecular structures of polysaccharides.

to have no effect on absorption to polymer materials of the membrane, so that the molecular weight cut-off can be determined by their removal.

The molecule of disinfection by-products and pharmaceutical active compounds exhibited a much lower removal than polysaccharides at the similar molecular weight of target solutes. This phenomenon would associate another consideration of factors except steric hindrance effect.

3.6. Consideration of Transport Phenomena through Nanofiltration

At this point, K_s for each compounds was further considered to clarify transport phenomena of disinfection by-products and pharmaceutical active compounds. The removal characteristics of polysaccharides were utilized to determine base factors such as molecular weight cut-off and porosity by curve fitting with model calculation. The factor K_s mean the correction factor of diffusion and convection term on the basis of steric hindrance effects. Therefore, the meaning of K_s would be another interaction between membranes and target solutes.

Fig. 9 showed the correlation of K_s with stokes radius of disinfection by-products and pharmaceutical active compounds during nanofiltration. Considering molecular weight is corresponded to removal of disinfection by-products and pharmaceutical active compounds, their removal characteristics through nanofiltration membranes are thought to be related to molecular size of them. In the condition of hydrodynamic fluid through membranes, molecule size of solute is often evaluated by Stokes radius. As a result, K_s was corresponded to solute radii. Estimation of K_s was possible by using radius of target solutes.

K_s was increased with an increase in solute size represented by Stokes radius for disinfection by-products and pharmaceutical active compounds. With this view, comparison of solute volume with pore volume would be available to interpret transport phenomena inside nanofiltration membranes. If porosity was fixed to a certain membrane, smaller volume of solute have lower K_s so that its removal come to be lower because movement of solute inside membrane is relatively free and solute flows through membrane with fluid. On the other hand, larger volume of solutes had higher K_s , and their removal came to be higher. Therefore, K_s was utilized in hindrance correction factor in the

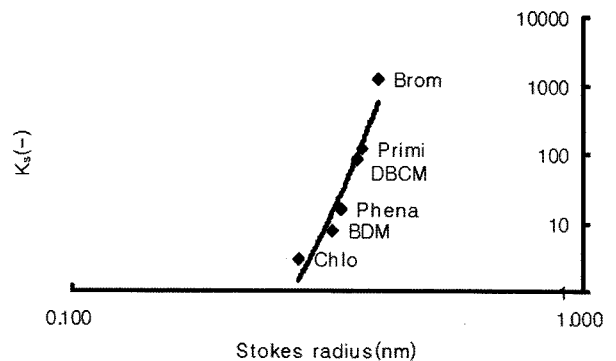


Fig. 9. Correlation of K_s with stokes radius of disinfection by-products and pharmaceutical active compounds during nanofiltration.

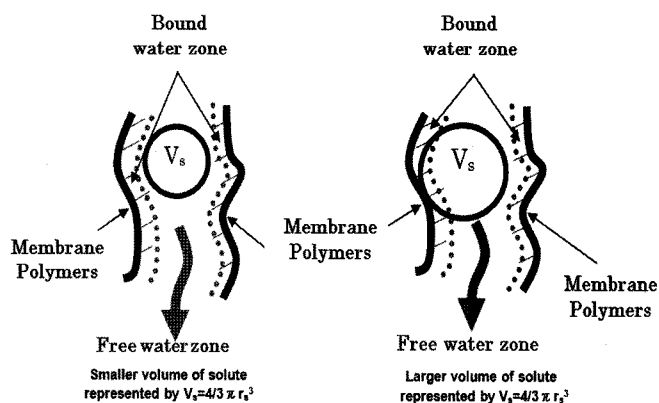


Fig. 10. Image of transport phenomena inside nanofiltration considering structure of membrane polymers.

diffusion-convection equation.

Considering K_s was corresponded to size of solute, the image of transport mechanism inside nanofiltration was discussed as follows. Nanofiltration membrane is assumed that it has pores, but its pore size varied, and pore is not cylindrical straight. When a solute flows through membrane polymer matrix which has pore size distribution, two types of fluid zone might combine flow region. One is free water zone and the other is bound water zone. Free water means that fluid can easily flow through membrane with less friction by the polymer matrix. On the other hand, bound water zone exist near the polymer matrix so that friction by membrane wall was relatively high.^{16,17)}

Fig. 10 shows schematic representation of flow of solute inside polymer membrane on the basis of K_s model. If a solute exists in free water zone, it easily flows through membrane with free water. But, if a solute exists in bound water zone, replacement of water by solute must occur, so that the flow of solute is retained comparing to free water.

The water zone, where a solute exists, can be determined by volume of a solute. A small volume of solute is easy to exist in free water. Friction of them to the polymer matrix is lower than that of a large one. Their removal by membrane, which consists of polymer matrix, comes to be lower.

4. Conclusions

Removal characteristics of the micro organic compounds such as disinfection by-products, pharmaceutical active compounds and polysaccharide by low-pressure nanofiltration process were investigated. In the case of conventional steric hindrance model, the removal characteristics of micro-organic compounds were not well explained. In this study, the factors affecting on removal of micro organic compounds such as disinfection by-products and pharmaceutically active compounds by low-pressure nanofiltration were determined by comparison of hindrance correction factor, K_s with experimental removal of target solutes. Consequently, the transport mechanism of micro organic compounds inside nanofiltration was discussed by using the correlation of membrane polymer matrix, which has pore size distribution with types of fluid zone inside nanofiltration membranes.

Nomenclature

C_i	: concentration of the i th solute in bulk solution (mol/L)
D_i	: diffusion coefficient of the i th solute (m^2/s)
J_i	: flux of the i th ion through the membrane ($m^3/m^2 \text{ sec}$)
J_v	: volume flux ($m^3/m^2 \text{ sec}$)
J_s	: flux of solute through the membrane ($m^3/m^2/\text{sec}$)
K_D	: averaged distribution coefficient of the i -th ion under diffusion conditions
K_F	: averaged distribution coefficient of the i -th ion under convection conditions
K_S	: corrected hindrance coefficient, function of solute radius
T	: temperature (K)
c_i	: concentration of the i th solute inside membrane (mol/L)
r_{si}	: stokes radius of the i th solute (nm)
r_s	: radius of solute (nm)
r_p	: radius of membrane pore (nm)
x	: distance inside the membrane (m)
R	: gas constant($= 8.31 \cdot 10^3 \text{ Nm/kgmolK}$)

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