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Removal of taste and odor model compounds (2-MIB and geosmin) with the NF membrane

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ABSTRACT

The objectives of this research were to identify seasonal variations of 2-MIB and geosmin which have been one of the biggest problems in the drinking water in the Han River in Korea and to evaluate the performance of the loose and tight NF membranes with respect to 2-MIB and geosmin rejection. Two kinds of NF membranes with different NaCl rejections were compared using a batch stirred cell to determine the membrane flux and the solute rejection for feed water. The results of the analysis of the occurrence characteristics of 2-MIB and geosmin, the major taste and odor material in the Han River water system show that the occurrence of 2-MIB continued from winter to spring (January–May) and through autumn (August–September), whereas geosmin occurred for about one to two weeks from summer to autumn (July–September) and spring (March–April). Following the rejection test of the taste and odor using the loose and tight NF membranes, it appeared that the two showed high rejection rates of 98% and above, irrespective of their concentration factor. The rejection of 2-MIB and geosmin increased with increasing shear rates for all of the NF membranes tested. Hydrodynamic operating conditions greatly affect the rejection of solutes in NF treatment. The rejection of taste odor compounds should increase with increased shear rates near the membrane surface. This suggests that the rejection will be further improved using dynamic membrane filtration.

Keywords: NF membrane; Taste and odor; Concentration polarization

1. Introduction

The factors that affect the taste and odor of tap water are broadly classified into chemical materials in sewage and wastewater, the inflow of byproducts of algae, aquatic animals and plants, and water sterilization agents [1]. Among them, the taste and odor compounds of the Han River water system are 2-MIB and geosmin, which cause the musty and earthy smell of water. These materials do not adversely affect human health, although they cause sensuous discomfort, which leads to the lessened use of the tap water. The odor thresholds of human beings with respect to these materials differ, but geosmin and 2-MIB are reported at 4 ng/L and 9 ng/L, respectively [2,3]. Accordingly, even a small amount of such materials can cause consumer complaints when they are not carefully

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handled in the water purification process [4]. At present, most of the water purification facilities under the Han River water system employ conventional water treatment methods that focus on coagulation–sedimentation–sand filtration. Moreover, the injection of chlorine and powdered activated carbon (PAC) contributes to the partial rejection of taste and odor causing substances, although their full removal is difficult. Their occurrence at a certain degree of concentration or above makes them difficult to deal with via prompt and sure responses. The objectives of this research were to identify seasonal variations of 2-MIB and geosmin which have been one of the biggest problems in the drinking water in the Han River in Korea and to evaluate the performance of the loose and tight NF membranes with respect to 2-MIB and geosmin rejection. Furthermore this study aims to analyze the rejection characteristics of 2-MIB and geosmin with the application of the solution-diffusion model, while considering the concentration polarization, to forecast the rejection characteristics of the water taste and odor materials within a wide range of operating conditions.

2. Theory

To predict the performance of the membrane under various operating conditions after analyzing the test results, the solution-diffusion model was applied while considering the concentration polarization. According to the solution-diffusion model, solvent flux and solute flux can be defined as follows [5]:

$$J_v = L_v\left(\Delta P - \Delta\Pi_{C_b}\right) \tag{1}$$

$$J_s = L_s\left(C_b - C_p\right) \tag{2}$$

where L_v is the solvent transport parameter, L_s is the solute transport parameter, C_b is the solute concentration in the bulk solution, C_p is the solute concentration at the permeate side, $\Delta\Pi_{Cb}$ is the osmotic pressure at the solute concentration of C_b and ΔP is the transmembrane pressure.

As filtering proceeded, however, concentration polarization occurred. Using C_m (the solute concentrations at the membrane surface) instead of C_b, the above equations can be modified into the following [5]:

$$J_v = L_v\left(\Delta P - \Delta\Pi_{C_m}\right) \tag{3}$$

$$J_s = L_s\left(C_m - C_p\right) \tag{4}$$

C_m is calculated according to the film theory to interpret the concentration polarization, and the solvent concentration profile on the surface can be calculated according to the following equation [5]:

$$\frac{C_m - C_p}{C_b - C_p} = e^{\frac{J_v}{k}} \tag{5}$$

where k is the mass transfer coefficient for the back diffusion of the solute from the membrane to the bulk solution on the high-pressure side of the membrane [6].

In a stirred cell, the growth of the concentration boundary layer is limited by stirring according to the mass transfer coefficient, using the following equation [7]:

$$k = 0.104\left(\frac{D_{sw}}{r}\right)\left(\frac{wr^2\rho}{\mu}\right)^{2/3}\left(\frac{\mu}{\rho D_{sw}}\right)^{1/3} \tag{6}$$

where r is the stirring radius, w is the stirring speed, μ is the liquid viscosity, ρ is the solution density and D_{sw} is the diffusion coefficient of the solute.

Using the above equations, L_v and L_s can be obtained from the experiment data to model the rejection under various conditions. L_v is easily determined from the measured pure water flux and Eq. (1). L_s is somewhat more difficult to estimate because the solute concentration at the membrane surface (C_m) is not known. In this study, the value of C_m was calculated using the shooting method, a type of numerical analysis to make the difference below 1%, between the solvent flux J_v that is calculated using the solution-diffusion model and the solvent flux J_v by the concentration polarization, with the initial value of C_m assumed to be identical to that of C_b.

3. Materials and methods

3.1. Membrane filtration

Using the batch-stirred cell, the test on the rejection characteristics of taste and odor causing materials was conducted in loose and tight NF membranes (NE70-loose NF and NE90-tight-NF, Woongjin) with different NaCl rejection. Feed water was made by diluting 2-MIB and geosmin stock in the MF membrane permeate using the Han-River water as raw water with a pore size of 0.01 μm (H2L, Korea). Table 1 presents the characteristics of the water quality of the MF permeate that was used as feed water in the test.

Table 2 shows the characteristics of the NF membranes that were used in the study. These two membranes belong to the thin film composite (TFC) with polyamide type in terms of quality. The NaCl rejection by the loose NF membrane, NE70 ranged from 40% to 70% but the tight

Table 1
Characteristics of the quality of the feed water used in this study

Items	Value
Turbidity, NTU	0.03–0.05
DOC, mg/L	1.5–1.8
UV254, abs./cm	0.019–0.023
TDS, mg/L	55–60

Table 2
List of NF membranes and their characteristics that were obtained from their manufacturers

Product name	NE70	NE90
NaCl rejection, %	40–70	85–95
$MgSO_4$ rejection, %	99.5	99.5
Membrane type	Thin-film composite	
Membrane material	PA (polyamide)	
Membrane surface charge	Negative	

NF membrane, NE90 provides high efficient NaCl rejection above 85%.

As shown in Fig. 1, the filtration tests were carried out in the batch type using the stirred cell that easily controls shear stress. The radius of the stirred cell module was set at 70 mm, with the filtration size at 300 mL. A magnetic stirrer (Stirrer Assembly 8200, Millipore, USA) was positioned just above the membrane. The length of the stirring bar was 68 mm. The operating pressure was adjusted with nitrogen gas and set at 4 bar.

A fresh membrane was first rinsed by letting it float skin-side down in distilled water for 30 min. Then it was placed in the stirred cell. The permeate flux was consecutively measured using the balance (Ohaus, UK) that was connected to the computer. The permeate flux was calculated by dividing the gradient of the time-permeate by the membrane areas. The concentration factor (F_c) is defined as the ratio of the feed volume to the concentrate volume, a factor that indicates the degree of concentration, as follows:

$$F_c = \frac{V_F}{V_C} = \frac{V_F}{V_F - V_P} \quad (7)$$

where V_F is the feed volume, V_C is the concentrate volume and V_P is the permeate volume.

3.2. Sample preparation

2-MIB and geosmin were chosen as the model taste and odor causing compounds in this study. They were purchased from Supeloco (Supelco, USA) in liquid form. The properties of the 2-MIB and geosmin are summarized in Table 3. Stock solutions of the 2-MIB and geosmin were prepared in methanol, and then diluted with the MF permeate.

3.3. Analytical methods

The headspace solid-phase micro-extraction (HS-SPME)/GC-MS was used to quantify the 2-MIB and geosmin concentrations. Sodium chloride, which was added prior to the extraction, was dried at 105°C for 1 h before it was used. The SPME fiber that was used in the experiment was 100 μm of poly dimethylsiloxane (Supelco, USA). The volume of the headspace vials was 25 mL, and aluminum caps with PTFE-coated silicone septa were used. GC/MS, which was equipped with both SPME (Polaris Q, Thermo Electron Corporation) and a fused silica capillary column (Chrompack sil-5MS, Varian, USA) was used to detect the samples at low concentrations (ng/L). The carrier gas (He) flow rate and oven temperature were 1.0 ml/min and 200°C, respectively.

4. Results and discussion

4.1. Characteristics of the 2-MIB and geosmin in terms of their seasonal occurrence in the Han River water system

Fig. 2 shows the variations in the 2-MIB and geosmin in the raw water from the Han River. The 2-MIB and geosmin in the raw water significantly changed with time. The 2-MIB occurrence was high in spring time (from January to May), and the geosmin occurrence was high in summer time (July).

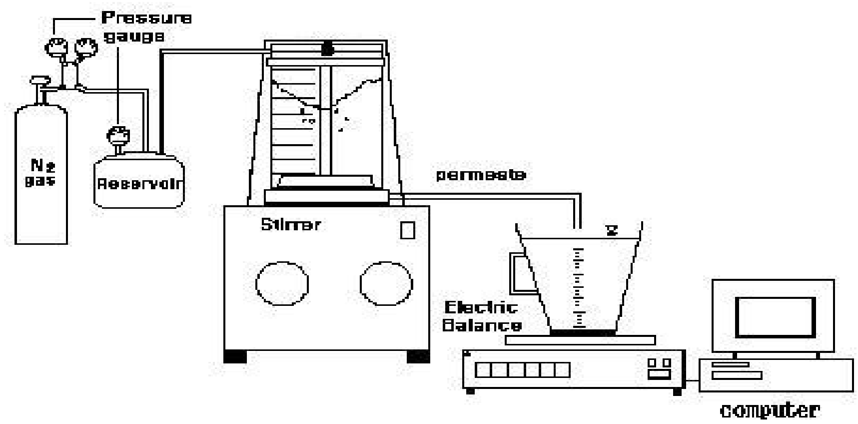
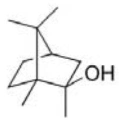
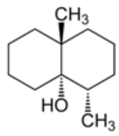


Fig. 1. Schematic diagram of the stirred cell NF device.

Table 3
Structure and physicochemical properties of the target compounds

Compounds	Chemical structure	Molecular weight (g/mol)	Chemical formula	log K_{ow}	Category
2-MIB		168.3	$C_{11}H_{20}O$	3.13	Musty
Geosmin		182.3	$C_{12}H_{22}O$	3.70	Earthy

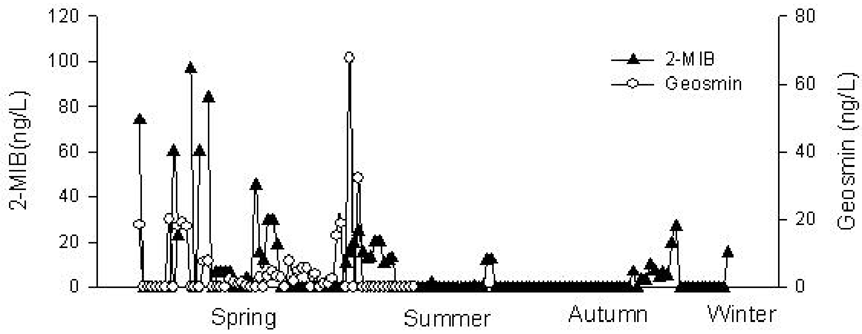


Fig. 2. Seasonal variations of the taste and odor compounds in the raw water.

Table 4 lists the results of a statistical analysis of the 2-MIB and geosmin in raw water in 2008. As can be seen, there was much variability throughout the experiment period, with the raw water 2-MIB varying between 0–84 ng/L and the raw water geosmin varying between 0–67.4 ng/L.

Table 4
Characteristics of the quality of the water used in this study

Items	No.	Std. dev.	Average	Min.	Max.
2-MIB, ng/L	150	15.705	6.60	n.d	97.0
Geosmin, ng/L	150	7.99	3.20	n.d	67.4

4.2. Rejection characteristics of 2-MIB and geosmin

Table 5 and Table 6 show the test conditions of the 2-MIB and geosmin rejection characteristics using loose and tight NF membranes (NE70-loose NF and NE90-tight-NF, Woongjin) with different NaCl rejections. Each test was conducted under a total of four conditions, that is, two kinds of concentration conditions (high concentration and low concentration) with two kinds of agitation speed (100 rpm and 200 rpm).

Fig. 3 shows the initial feed solution and the concentration and rejection rates of the 2-MIB and geosmin of the permeate according to the concentration factor. The test results show that NE70 and NE90 showed high levels of

Table 5
Test conditions for the 2-MIB and geosmin rejection characteristics using the loose NF membrane, NE70

	2-MIB (ng/L)		Geosmin (ng/L)	
Stirring speed (rpm)	Low concentration	High concentration	Low concentration	High concentration
100	21.3	76.4	31.4	120.1
200	35.9	116.4	51.9	90.3

Table 6
Test conditions for the 2-MIB and geosmin rejection characteristics using the tight-NF membrane, NE90

	2-MIB (ng/L)		Geosmin (ng/L)	
Stirring speed (rpm)	Low concentration	High concentration	Low concentration	High concentration
100	25.50	148.11	42.39	95.98
200	29.30	97.40	38.13	100.37

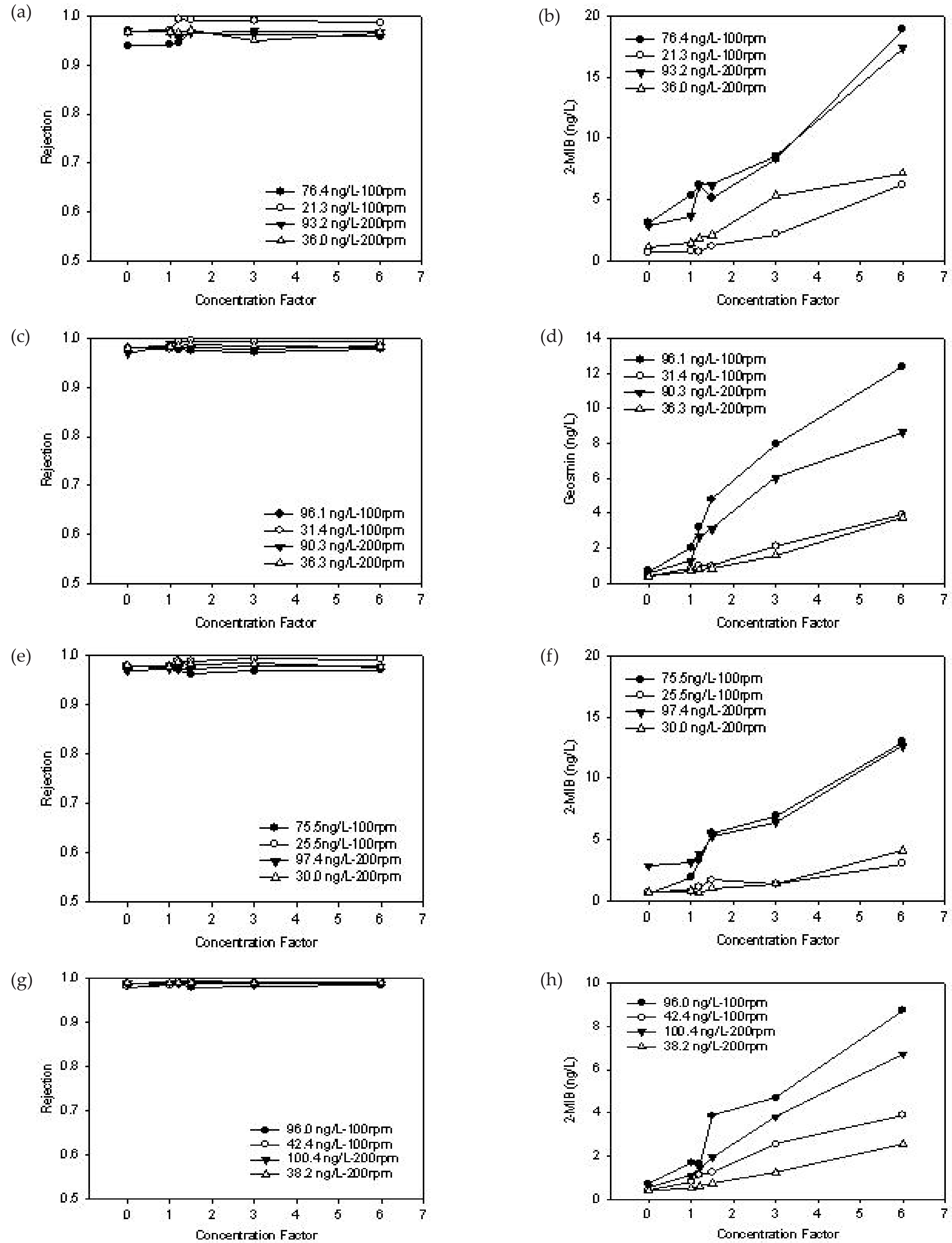


Fig. 3. Concentrations of the 2-MIB and geosmin in the permeate according to the concentration factor and the agitation speed. (a) 2-MIB rejection by NE-70; (b) 2-MIB concentration of the NE-70 permeate; (c) Geosmin rejection by NE-70; (d) Geosmin concentration of the NE-70 permeate; (e) 2-MIB rejection by NE-90; (f) 2-MIB concentration of the NE-90 permeate; (g) Geosmin rejection by NE-90; and (h) Geosmin concentration of the NE-90 permeate.

rejection of 2-MIB and geosmin under all test conditions. It also appeared that as the concentration of the target compound in the feed water became lower and the stirring speed became faster, the rejection rates increased. Moreover, the results show that as the concentration factor increased, so did the concentration of the permeate. This seems to be attributable to the increase in the concentration of the target compound in the feed solution and the decrease in the rejection rates.

It appeared that the 2-MIB exceeded its odor threshold of 9 ng/L only under high-concentration conditions of the two kinds of membranes, with a 100-rpm stirring speed and a concentration factor of 3 or above, as well as with a 200-rpm stirring speed and a concentration factor of 3 or above. As for the geosmin, it also appeared to have exceeded its odor threshold of 4 ng/L under high concentrations with a 100-rpm stirring speed and a concentration factor of 2 or above, as well as with a 200-rpm stirring speed and a concentration factor of 3 or above.

Fig. 4 shows the changes in the permeate flux under all test conditions. It appeared that as the concentration factor increased, the permeate tended to decrease. When the concentration factor was set at 6, it decreased by approximately 3 LMH compared with the initial flux. This seems to have been due to an increase in the osmotic pressure, as the concentration of the TDS (total dissolved solid) in the MF permeate, which was used as the feed solution, was enriched according to the concentration factor.

Fig. 5 shows the fitting of the test results and the analysis results to the solution-diffusion model, while considering the concentration polarization. For each taste and odor model compound, the model calculation was performed to find the parameter (L_s) that will minimize the difference between the model predictions and the experiment results under different experiment conditions using the residual constant R^2 [8].

$$R^2 = \frac{\sum_{i=1}^{N}\left(C_{P_{m,i}} - C_{P_{e,i}}\right)^2}{\sum_{i=1}^{N}\left(C_{P_{m,i}} - \overline{C_{P_{m,i}}}\right)^2} \quad (8)$$

where N is the total number of experiment data, $C_{P_{m,i}}$ is the i^{th} value for the calculated permeate concentration, $\overline{C_{P_{m,i}}}$ is the average value for the calculated permeate concentration and $C_{P_{e,i}}$ is the i^{th} value for the experimental permeate concentration.

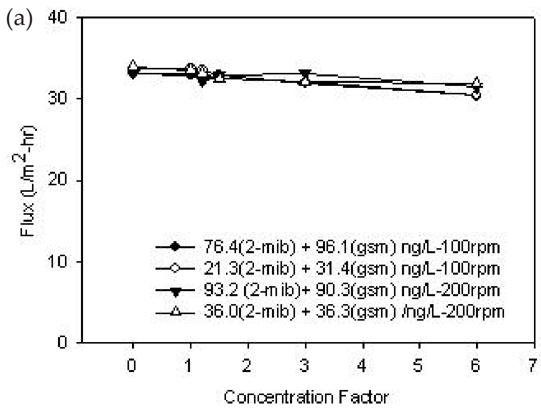
It appeared from the fitting that the test results and the model are relatively matched. As shown in Table 7, the solvent transport parameter and the solute transport parameter were calculated.

4.3. Theoretical model for performance prediction

Fig. 6 shows the contours of the constant rejection of 2-MIB and geosmin as a function of the stirring speed and the effective transmembrane pressure. As expected, the best rejection occurred at high stirring speeds and high transmembrane pressures. The dependence of the rejection on the stirring speed and the transmembrane pressure was not linear, though. The closely spaced contours at low stirring speeds and low transmembrane pressures indicate a much stronger dependence under these conditions. This suggests that the optimal operating conditions are near the elbow of the contours at moderate stirring speeds and transmembrane pressures rather than at extreme values for these conditions. For example, the 2-MIB rejection by NE70 (Fig. 6a) is about 96.7% at 3.0 bar and 300 rpm. Increasing the transmembrane pressure until 10.0 bar increases the rejection by less than 1%. Likewise, increasing the stirring speed until 1000 rpm

Table 7
Solvent and solute transport coefficients of NE70 and NE90

Membrane	Transport parameters	2-MIB	Geosmin
NE 70	L_v, m²s/kg	2.35e-11	2.35e-11
	L_s, m/s	1.80e-7	9.50e-8
NE 90	L_v, m²s/kg	2.55e-11	2.52e-11
	L_s, m/s	1.30e-7	6.50e-8



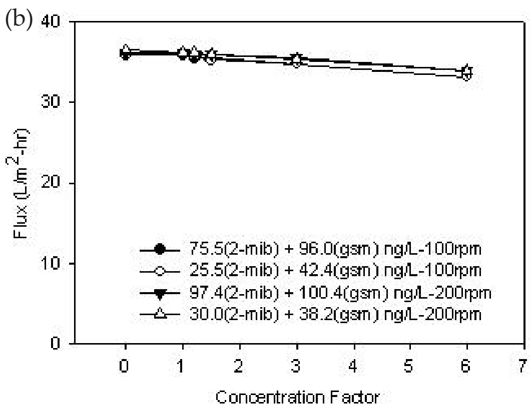


Fig. 4. Changes in the flux in the permeate according to the concentration factor and the agitation speed, (a) NE-70; and (b) NE-90.

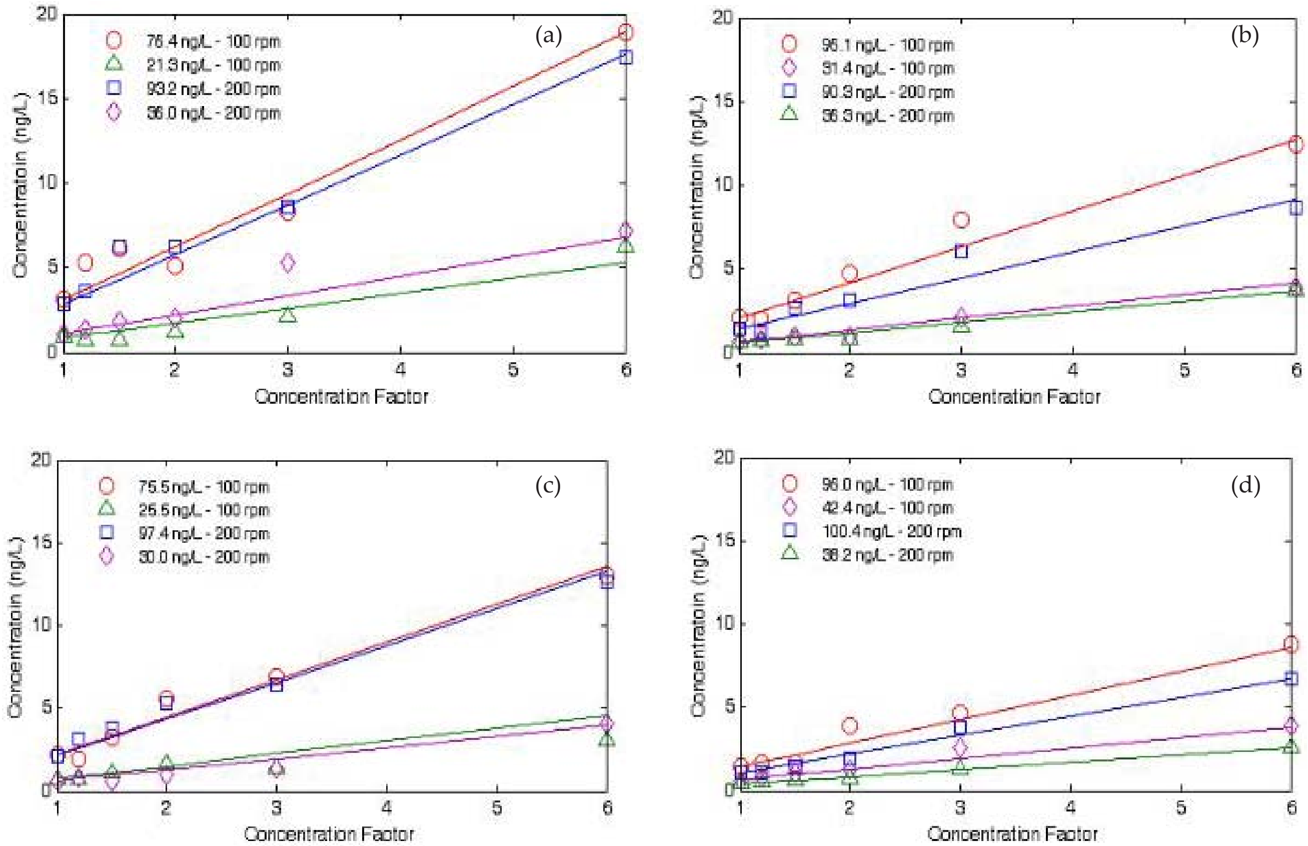


Fig. 5. Result of the fitting based on the test results for the 2-MIB and geosmin, and the model equation. (a) 2-MIB concentration of the NE-70 permeate; (b) geosmin concentration of the NE-70 permeate; (c) 2-MIB concentration of the NE-90 permeate; and (d) geosmin concentration of the NE-90 permeate.

only raises rejection to a little over 97.7%. Increasing both transmembrane pressure and stirring speed only brings the rejection to a little over 97.7%.

5. Conclusions

The results of the analysis of the occurrence characteristics of 2-MIB and geosmin, the major taste and odor material in the Han River water system, show that the occurrence of 2-MIB continued from winter to spring (January–May) and through autumn (August–September), whereas geosmin occurred for about one to two weeks from summer to autumn (July–September) and spring (March–April). Thus, fundamental measures are needed to address the occurrence of the taste and odor materials as the issue appears for a long period of about seven months out of 12 months.

Following the rejection test of the taste and odor using the two kinds of TFC NF membranes, it appeared that the two showed high rejection rates of 98% and above, irrespective of their concentration factor. The test results also showed that geosmin exhibited somewhat higher rejection rates than MIB in the two membranes. The NE90 membrane showed a higher flux and a higher rejection rate than the NE70 membrane, although the difference was insignificant.

Under the concentration factor of 3 or lower, the concentrations of 2-MIB and geosmin in permeate water were high concentration (approximately 100 ng/L) and the low stirring speed appeared to have been below the human odor threshold. Accordingly, when introducing NF membrane processing in water treatment plants, 2-MIB and geosmin in permeate water will be detected for a longer period of time. It is assumed that prompt and sure responses to occasional detection of high concentrations of 2-MIB and geosmin will be possible.

It was also seen that the application of the solution-diffusion model, while considering the concentration polarization is effective in predicting the characteristics of the NF membrane in eliminating the foul-taste- and odor-causing material.

The results of the model analysis show that the hydrodynamic operating conditions greatly affect the rejection of solutes in the NF treatment. The rejection of the taste and odor compounds should increase with increased shear rates near the membrane surface. This suggests

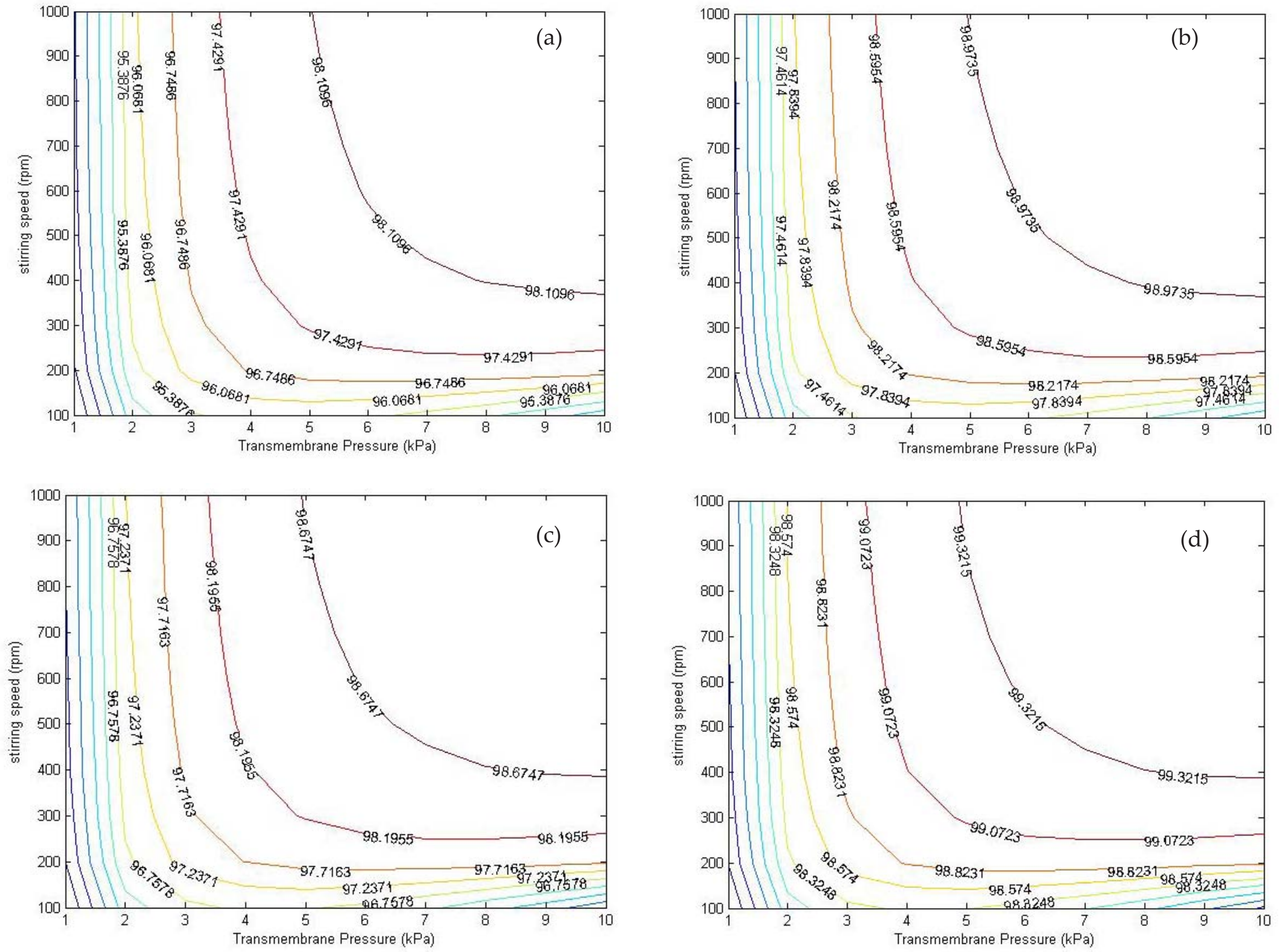


Fig. 6. Contour diagrams of the 2-MIB and geosmin rejection at different pressures and stirring speeds. Modeling condition: concentration = 100 ng/L. (a) 2-MIB rejection by NE-70; (b) Geosmin rejection by NE-70; (c) 2-MIB rejection by NE-90; and (d) geosmin rejection by NE-90.

that the rejection will be further improved using dynamic membrane filtration.

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