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Evaluation of membrane fouling mechanism in various membrane pretreatment processes

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ABSTRACT

Pretreatment of organic matter with coagulation and MIEX® was evaluated using bench-scale experimental procedures on NOM to determine its effect on subsequent UF or MF membrane filtration. Moreover, this work determines the membrane fouling mechanisms according to membrane pretreatment conditions. When applying the MIEX® process as a pretreatment, flux decline was significantly higher than that of the coagulation process. The flux decline curves for MF membranes are very different from the curves for UF membranes presented earlier. It is very interesting that while the MIEX®–UF process shows much higher removal of DOC than that of coagulation, the rate of flux decline was significantly greater. In addition, when comparing coagulation with MIEX®, coagulation caused a lower rate of flux decline for both hydrophilic and hydrophobic membranes due to enhanced formation of flocs. The permeate flux rapidly declined due to simultaneous pore blocking and cake formation. Also, the permeate flux declined with decreasing internal pore size resulting from particle deposition into the membrane pore. In addition, the experimental results prove that the MIEX® and coagulation pretreatment significantly reduced the fouling of the membrane. Especially, the combination of MIEX®+coagulation pretreatment significantly reduced membrane fouling. Consequently, applying a pretreatment process before UF was found to be very effective in fouling reduction as well as critical flux increase.

Keywords: NOM; Membrane fouling; Coagulation; MIEX®; Pretreatment

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1. Introduction

Since membrane technology has been applied for water and wastewater treatment, it has grown steadily with public demand for high water quality and strict regulation [1]. Natural organic matter (NOM) poses a problem in water treatment for a number of reasons. One of the critical problems encountered during the membrane process in drinking water treatment is irreversible fouling through an adsorption of NOM [2]. Several authors described NOM as one of the major membrane fouling agents in microfiltration (MF), ultrafiltration(UF) and nanofiltration (NF) of surface water [3–7]. However, in a membrane process, the permeate flux of water declines due to the fouling induced by colloidal particles and NOM on the membrane surface, and the lifetime of membranes also decreases because of consequent frequent washing. Therefore, extensive research has been conducted on the role of NOM and its characteristics on the fouling of membranes [8,9].

Generally, coagulation and powdered activated carbon (PAC) processes have been used as pretreatment process. Recently, the ion-exchange resin method has been high-

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lighted as a pretreatment process. As compared with conventional ion-exchange resin, the magnetic ion exchange resin (MIEX®) has a relatively high specific surface area and a fast reaction rate with NOM [10–12]. In this study, pretreatment of organic matter with coagulation and MIEX® was evaluated using bench-scale experimental procedures on NOM to determine its effect on subsequent UF or MF membrane filtration. Moreover, this work determines the membrane fouling mechanisms according to membrane pretreatment conditions.

2. Materials and method

2.1. Raw water

Raw water was collected from the downstream of the Nakdong River, which is used as a drinking water source for the city of Busan in Korea. In order to increase NOM concentration, the raw water was double concentrated at 30 using a rotary evaporator (R205, Büchi, Germany). Table 1 summarizes characteristics of the concentrated water. Only NOM was filtered through a 0.45 µm filter paper before experiments. NOM + particles were not filtered through a filter paper.

2.2. Experimental procedure

The coagulation and MIEX® experiments were conducted using a 2 L jar with jar-tester (PB-700, Phipps & Bird, USA). An aluminium salt coagulant, PSO-M (Al_2O_3 7%, Seojung Chemical, Korea), which is widely used at the water treatment facility in the Busan area, was used for this investigation. The raw water for coagulation was rapidly mixed at 250 rpm (G = 550 s^{-1})for 1 min after coagulant addition followed by slow mixing at 30 rpm for 5 min. Coagulation pH was ambient pH. For the MIEX® experiment, varying amounts of MIEX® were added to sample waters on a v/v basis, and 30 min of agitation at 100 rpm (G = 150 s^{-1})followed by 15 min of settling. For coagulant and MIEX dosage, 100 mg/L of coagulant was used for the optimum organic removal point. Also, 12 mL/L MIEX and 12 mL/L MIEX in combination with 20 mg/L coagulant was used for the optimum organic removal point.

Table 1
Characteristics of raw water and concentrated water

Item (unit)	Nakdong River water	Only NOM	NOM+ particles
Temp. (°C)	18–22	18–22	18–22
pH	7.4–7.8	7.2	7.6
Turbidity (NTU)	0.2–0.4	0.6	11
UV254 (cm^{-1})	0.051–0.056	0.103	0.104
DOC (mg/L)	3.6–4.0	4.64	4.64
SUVA (L/m mg)	1.21–1.4	2.31	2.25
Alkalinity (mg/L as $CaCO_3$)	45–50	66	64

Membrane tests were performed using a dead-end stirred filtration cell (Millipore, U.S.A.) that was connected to a feed reservoir and a nitrogen gas tank. The transmembrane pressure was regulated using nitrogen gas, and the permeate flow rate was determined by weighing the permeate on an electronic top-loading balance. The transmembrane pressure was maintained at 2 bar and 1 bar for UF and MF membranes, respectively. The UF membrane used for this test was hydrophilic regenerated cellulose (YM100, Millipore, USA) and hydrophobic polysulfone (PM100, Millipore, USA) with molecular weight cut-offs (MWCO) of 100 kDa. The MF membrane was hydrophilic mixed cellulose ester (GVHP, Millipore, USA) with a mean pore size of 0.22 µm. An aliquot of NOM was fractionated into humic and nonhumic fractions by employing the technique based on the adsorption of humic substances onto XAD-8 resin under acidic conditions (pH 2). The organics adsorbed on resin were subsequently eluted with NaOH (pH 12).

2.3. Filtration model

The origin of the flux decline can be accounted for by using four different theoretical kinetics models commonly employed for systems showing flux decline [13]. Hermia [14] introduced some filtration models: complete blocking, intermediate blocking, standard blocking, and cake filtration which aim to describe fouling mechanism [12]. The models are valid for unstirred, dead-end filtration, and complete rejection of solute by the membrane. The complete blocking model occurs when particles arrive at the membrane and block some pore or pores with no superposition of particles. An intermediate blocking model is when particles can settle on other particles previously arrived that already block some pores. A standard blocking model is when particles arrive at the membrane and are deposited onto the internal pore wall. The cake filtration model is when particles are located on other already arrived and are already blocking some pores. The models are valid for unstirred, dead-end filtration, and complete rejection of solute by the membrane. The filtration models applied in this study are summarized in Table 2.

3. Results and discussion

Fig. 1 shows the changes in permeate flux for UF(MF) alone, coagulation–UF (MF), MIEX®–UF(MF), and MIEX®–coagulation–UF (MF) processes, respectively. Overall, applying pretreatment process before UF membrane

Table 2
Constant pressure filtration models [15]

Model	Equation	Description
Complete blocking	$\ln J = -k_b\, t + \ln J_0$	Particles arriving to the membrane block some pore or pores with no superposition of particles.
Intermediate blocking	$J_0/J = (1 + k_i\, t)$	Particle can settle on other particle previously arrived and already blocking some pores or it can also directly block some membrane area.
Standard blocking	$J_0/J = (1 + k_s\, t)^2$	Particle arriving to the membrane was deposited onto the internal pore wall leading to a decrease in the pore volume..
Cake filtration	$J_0/J = (1 + k_c\, t)^{1/2}$	Particle locates on other already arrived and already blocking some pores and there is no room for a direct obstruction of any membrane area.

where J = permeate flux per membrane area at time; J_0 = initial permeate flux per membrane area at time 0, k_b = kinetic constants of complete blocking; k_i = kinetic constants of intermediate blocking, k_s = kinetic constants of standard blocking; and k_c = kinetic constants of cake filtration.

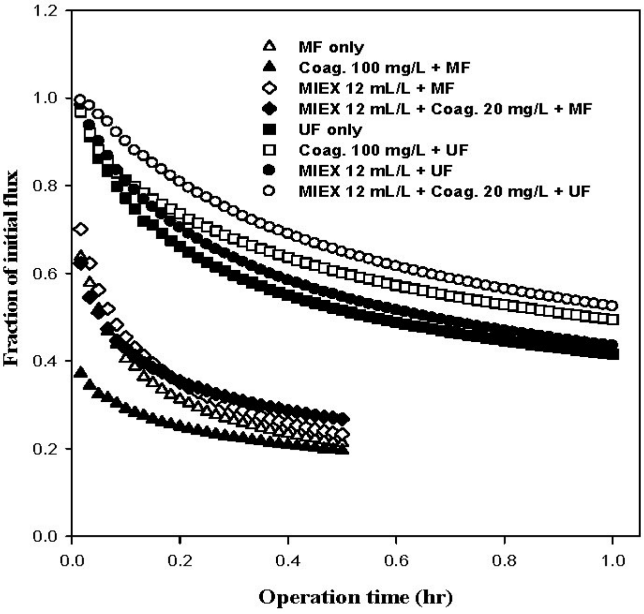

Fig. 1. Changes in permeate flux under various membranes and pretreatment processes using a NOM solution.

filtration induced lower flux decline. However, when using the MIEX® process as a pretreatment, the flux decline was significantly higher than that of the coagulation process. As shown Table 3, it is very interesting that while the MIEX®–UF process shows a much higher removal of DOC than that of coagulation, the rate of flux decline was significantly greater. The flux decline curves were obtained using a MF membrane with a larger pore size (0.2 μm) to see the fouling characteristics of NOM. The flux declines curves for the MF membrane are very different from the curves for the UF membrane presented earlier. That is, the coagulation–MF process results in the highest flux decline, while relatively lower flux decline has been shown for the MIEX®–UF process. From this result, it is suggested that in MF membrane, since the pore size is much larger than the MW of NOM fraction which remained after MIEX® treatment, the MF membrane was not fouled much by larger MW organic matter. Also, in coagulation–MF processes, the fine flocs formed by coagulation caused clogging that directly blocked the pores on the MF membrane rather than forming a cake layer on the surface of MF membrane. Jung and Kang [15] reported that due to the cake layers formed on membrane surface, the flux decline for the membrane with small pores was lower than that for the membrane with relatively larger pores [15].

Table 3
Comparison of organic fraction between raw water and treated water

	Hydrophilic matter (mg/L)	Hydrophobic matter (mg/L)
Raw water	1.8	2.7
MIEX® 12 mL/L + UF	0.75	0.5
Coag. 100 + UF	1.3	1.4
MIEX® 12 mL/L+ Coag. 20 + UF	0.6	0.4

Fig. 2 shows the changes in permeate flux for the UF membrane under various membrane materials without using particle water (only NOM). The UF membrane with MWCO 100 kDa was used and two different membrane materials (hydrophilic and hydrophobic) were used for the membrane experiment. For different pretreatment conditions, the samples were fed into the UF membrane after either MIEX® or coagulation. As shown in Fig. 2, the permeate flux significantly declined with UF alone after 30 min of UF operation. However, the coagulation–UF, MIEX®–UF, and MIEX®–coagulation–UF processes caused much less flux decline. In addition, the rate of flux decline for the hydrophobic membrane was significantly greater than for the hydrophilic membrane, regardless of pre-

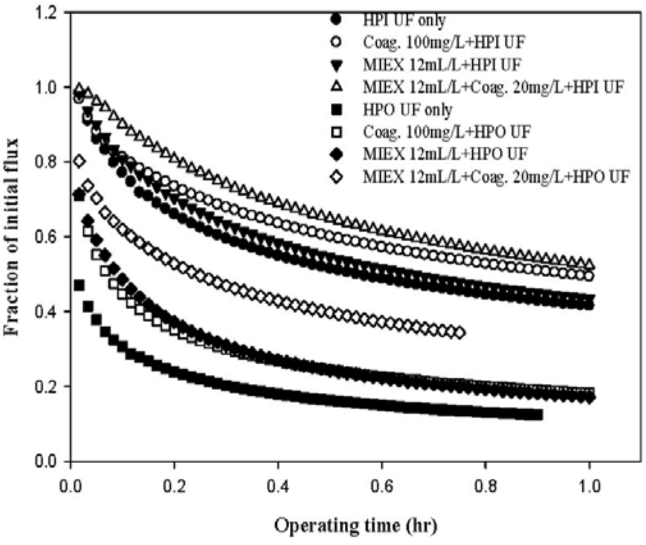

Fig. 2. Changes in permeate flux of UF membrane under various membrane materials (NOM).

treatment conditions used. When comparing coagulation with MIEX$^{®}$, coagulation caused a lower rate of flux decline for both hydrophilic and hydrophobic membranes due to enhanced formation of flocs. Furthermore, Fig. 2 indicates that coagulation pretreatment significantly reduced the fouling of the hydrophilic membrane, but caused a small decrease in the flux reduction of the hydrophobic membrane. Less flux decline caused by coagulation is considered to be due to the transformation of dissolved organics into particles that are easily removed by the size exclusion mechanism of UF. That is, during the coagulation process, substantial changes in dissolved organics must be occurred due to the simultaneous formation of microflocs and NOM precipitates. Wisner et. al. [16] also reported that cakes formed from humic acid destabilized with an aluminum coagulant have been found to present minimal specific resistance when humic acid is coagulated under conditions of precipitation/charge neutralization [16]. Therefore, aggregation of small colloids and dissolved organic matter by coagulation may lead to a larger effective particle size, which may result in less specific resistance.

The fouling mechanisms on the membrane surface and into its porous structure were analyzed in terms of several kinetic models [9,10]. In order to analyze the fouling kinetics, the various kinetic models described in Section 2.3 are used to fit the experimental results. Figs. 3–5 and Table 4 show the kinetic models and kinetic constants obtained for each operation condition. As shown Figs. 3–5, the permeate flux was rapidly decreased by simultaneous pore blocking and cake formation. Also, the permeate flux declined with decreasing internal pore size resulting from particle deposition into the membrane pore. This implies that all four fouling mechanisms are valid when applying these filtration models. In addition, the experimental results prove that MIEX$^{®}$ and coagulation pretreatment significantly reduced the fouling of the membrane. Especially, the MIEX$^{®}$+coagulation pretreatment process significantly reduced the membrane fouling. The kinetic constants, K_s, K_i, and K_c, derived from Figs. 3–5 are summarized in Table 4. The kinetic constants very well followed the defined tendencies for the pretreatment process and membrane properties. The results of analyzing in mechanisms on UF membrane fouling in applications of membrane materials and coagulation pretreatment process showed that values of kinetic constants (K_s, K_i and K_c) were higher for the hydrophobic membrane than for the hydrophilic membrane. However, the kinetic constant of K_c showed a higher value for the hydrophilic membrane and the constants K_s and K_i showed higher values for the hydrophobic membrane. For the combination of coagulation with UF processes, flocs led to fouling due to cake layer formation on the surface of the hydrophilic membrane, while microflocs and membrane surface fouling led to fouling on the surface of the hydrophobic membrane.

When the pretreatment process was applied, the kinetic constants, K_s, K_i, and K_c, showed lower values than those with UF alone. Consequently, applying a pretreatment process before UF was found to be very effective in fouling reduction as well as critical flux increase. Also, when using UF alone, K_s, K_i, and K_c showed higher values for the hydrophobic membrane. This suggests that the UF membrane fouling mainly caused an internal pore size decreasing due to adsorption of organic matter into the pore surface and by a gel layer formation on membrane surface of organic for hydrophobic membrane. In conclusion, the decrease in the pore volume, caused by the organic matter adsorption into the internal pore, was greater with the hydrophobic mem-brane than with the hydrophilic membrane.

Fig. 6 shows the changes in permeate flux for the UF membrane under various pretreatments using NOM + particle water. The UF membrane with MWCO 100 kDa was used and two different membrane materials (hydrophilic and hydrophobic) were used for membrane experiment. For different pretreatment conditions, the samples were fed into the UF membrane after either MIEX$^{®}$ or coagulation. As shown in Fig. 6, the permeate flux significantly declined with only UF after 30 min of UF operation. However, the coagulation–UF process caused much less flux decline. In addition, the rate of flux decline for the hydrophobic membrane was significantly greater than for the hydrophilic membrane, regardless of pretreatment conditions used. When comparing the NOM only sample and NOM + particles sample, NOM + particles had a lower rate of flux decline for both hydro-

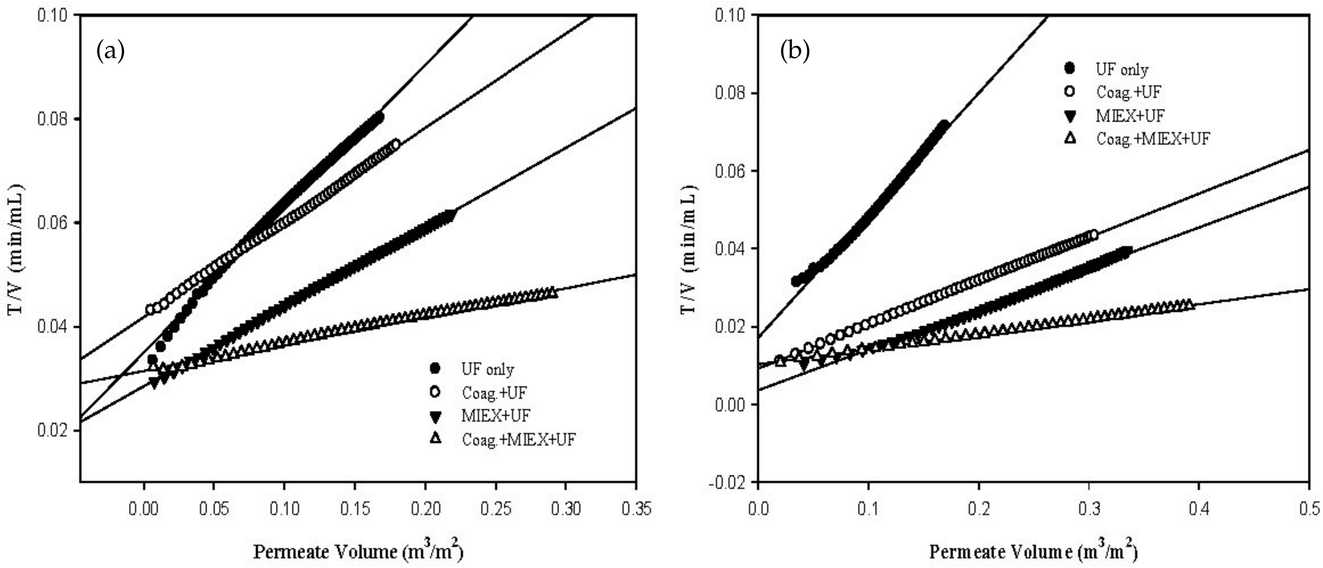

Fig. 3. Cake filtration model as a function of membrane materials and pretreatment type. (a) Hydrophilic UF membrane; (b) ydrophobic UF membrane.

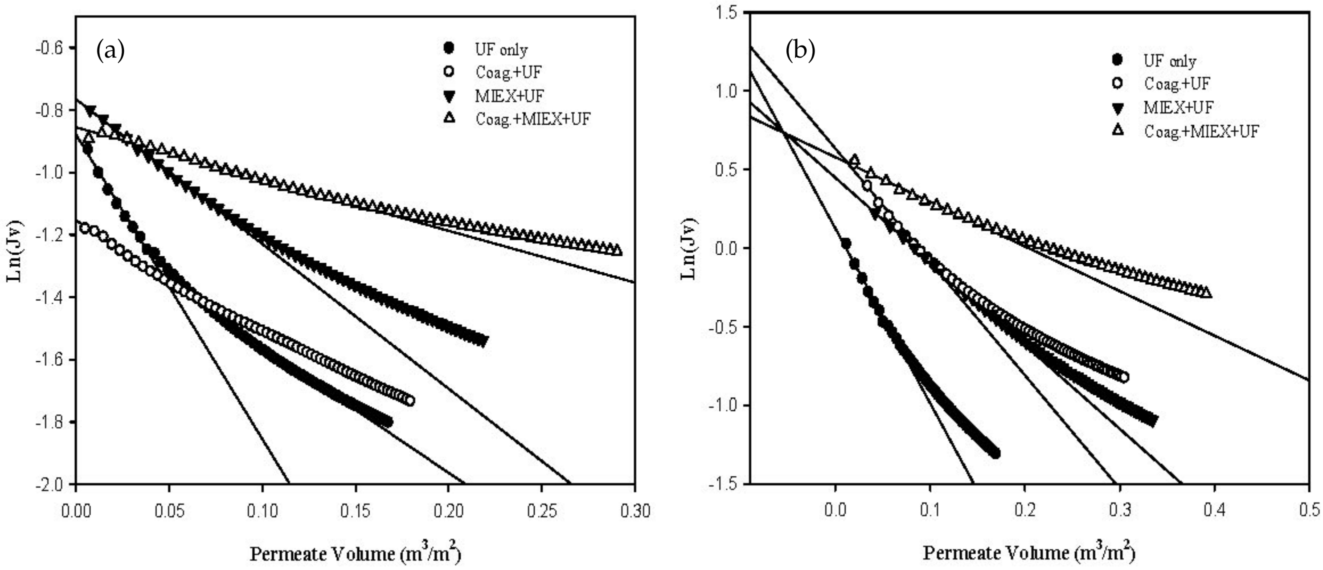

Fig. 4. Intermediate blocking model as a function of membrane materials and pretreatment type: (a) hydrophilic UF membrane; (b) hydrophobic UF membrane.

Table 4
Estimation of kinetic constant for each filtration model (NOM)

	UF only		Coag.+UF		MIEX®+UF		Coag.+MIEX®+UF	
	HPI	HPO	HPI	HPO	HPI	HPO	HPI	HPO
K_c (min/m^8)	0.28	0.31	0.18	0.11	0.15	0.10	0.05	0.04
K_i (m^{-1})	9.77	11.11	4.05	7.21	4.64	5.32	1.66	2.84
K_s (m^{-3})	0.81	1.87	0.66	1.09	0.66	1.18	0.34	0.78

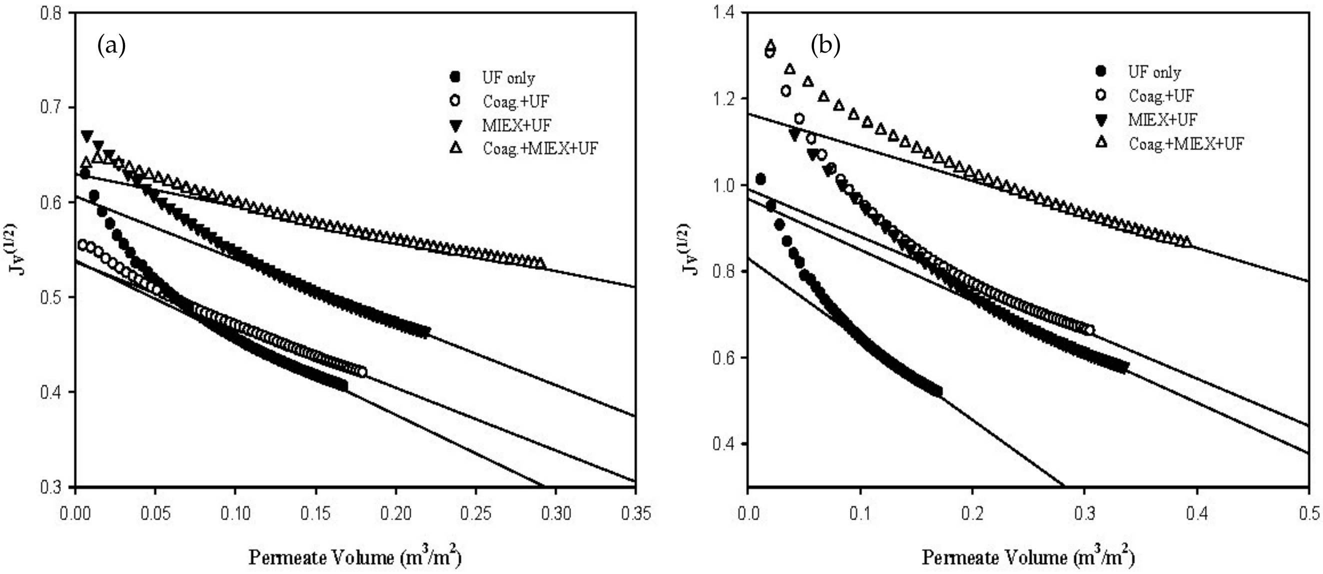

Fig. 5. Standard blocking model as a function of membrane materials and pretreatment type. (a) Hydrophilic UF membrane; (b) hydrophobic UF membrane.

Table 5
Estimation of kinetic constant for each filtration model (NOM + particles)

	UF only		Coagulation + UF		MIEX® + UF		Coagulation + MIEX® + UF	
	HPI	HPO	HPI	HPO	HPI	HPO	HPI	HPO
K_c (min/m^8)	0.34	0.18	0.18	0.02	0.15	0.10	0.05	0.01
K_i (m^{-1})	10.25	10.25	4.08	2.05	4.75	5.42	1.81	1.62
K_s (m^{-3})	0.93	1.61	0.66	0.46	0.77	1.54	0.35	0.45

philic and hydrophobic membranes due to enhanced formation of floc by particles.

The fouling mechanisms on the membrane surface and into its porous structure were analyzed in terms of several kinetic models. In order to analyze the fouling kinetics, the various kinetic models described in Section 2.3 are used to fit the experimental results. Figs. 7–9 and Table 5 show kinetic models and kinetic constants obtained for each operation condition. As shown Figs. 7–9, the permeate flux rapidly declined due to simultaneous pore blocking and cake formation. Also, the permeate flux declined with decreasing internal pore size resulting from particle deposition into the membrane pore. This implies that all four fouling mechanisms are valid when applying these filtration models. In addition, the experimental results prove that the MIEX® and coagulation pretreatment significantly reduced the fouling of the membrane. Especially, MIEX®+Coag pretreatment process significantly reduced the membrane fouling. The kinetic constants, K_s, K_i, and K_c, derived from Figs. 7–9, are summarized in Table 5. The kinetic constants followed very well the defined tendencies for pretreatment process and membrane properties. When the pretreatment process applied, the kinetic constants showed lower values than those with only the UF process. Consequently, applying a pretreatment process before UF was found to be very effective in fouling reduction as well as critical flux increase by reducing organic load and forming a cake layer on the membrane surface. Also, when using UF alone, K_s had a lower value for the hydrophobic membrane, while K_i and K_c showed higher values for the hydrophilic membrane. This suggests that UF membrane fouling occurred mainly due to the internal pore size decreasing due to adsorption of micro-particles onto the pore surface for the hydrophobic membrane, and by sieving of micro-particles and formation of a cake layer on the membrane surface for the hydrophilic membrane. It was shown that the fouling on the surface was relatively lower but the fouling on the pores was relatively higher when a combination of MIEX and UF processes was employed.

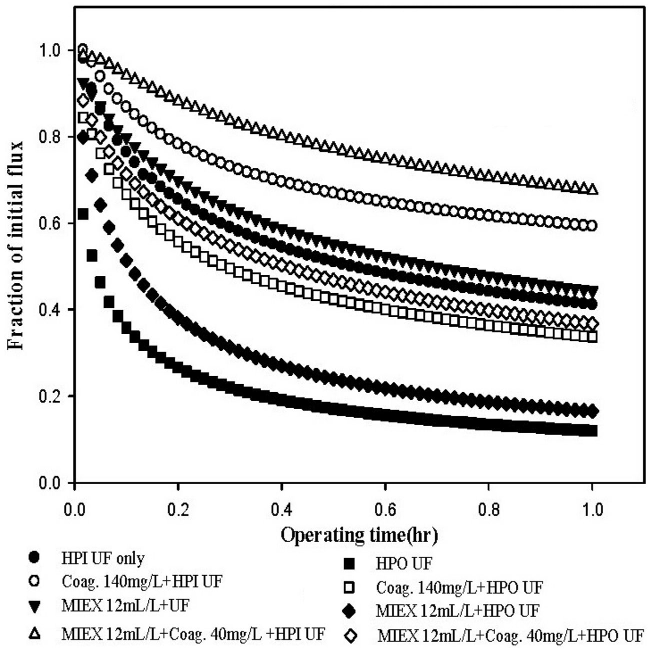

Fig. 6. Changes in permeate flux of UF membrane under various pretreatment conditions using NOM + particles.

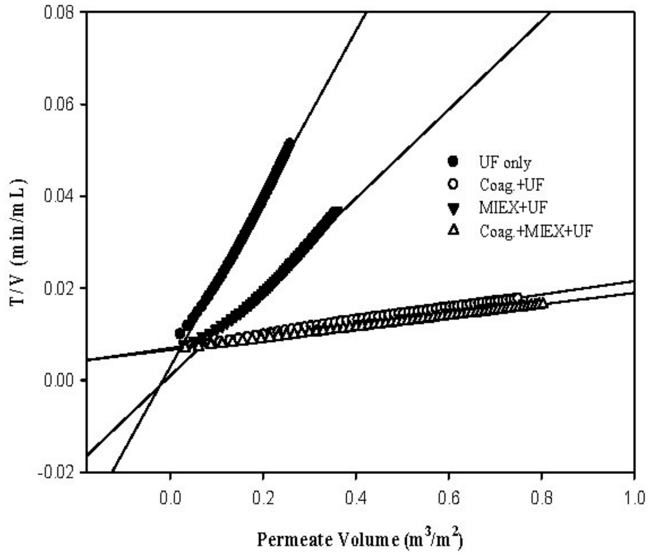

Fig. 7. Cake filtration model as a function of the hydrophobic membrane pretreatment process using NOM + particles.

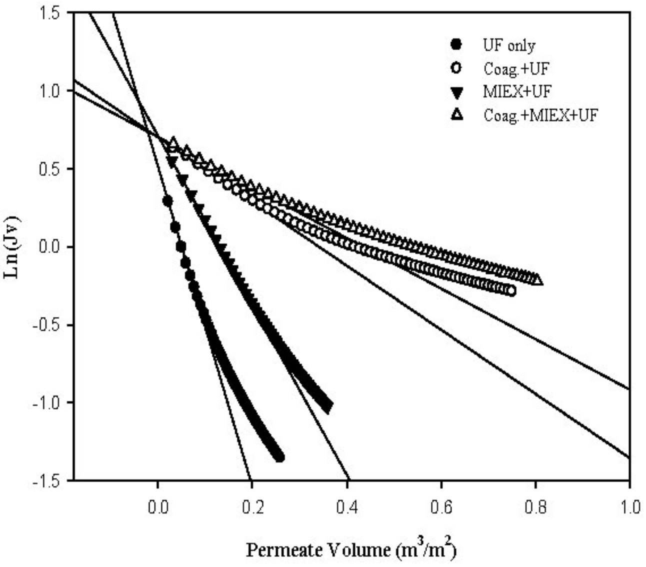

Fig. 8. Intermediate blocking model as a function of the hydrophobic membrane pretreatment process using NOM + particles.

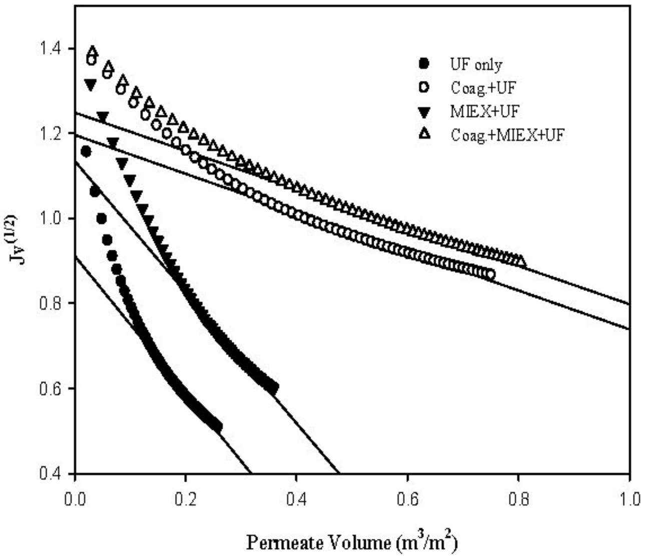

Fig. 9. Standard blocking model as a function of hydrophobic membrane. pretreatment process using NOM + particles.

In addition, values of kinetic constants of K_s, K_i and K_c were relatively low in MIEX according to lower organic loading rates and larger flocs formed in the coagulation process when MIEX + coagulation + UF processes were employed. This observation suggests that much less fouling on the surface and pores on the membrane made it quite less resistant for flux. In conclusion, the decrease in the pore volume, which was caused by the particle deposition into the internal pore, was greater with the hydrophobic membrane than with the hydrophilic membrane.

4. Conclusions

The flux decline curves for MF membranes are very different from the curves for UF membranes. That is, the coagulation–MF process results in the highest flux decline, while relatively lower flux decline has been shown for the MIEX®–UF process. When applying the MIEX® process as a pretreatment, the flux decline was significantly higher than that of coagulation. In addition, the experimental results prove that the MIEX® + coagulation membrane pretreatment reduced fouling of the membrane.

It is very interesting that while the MIEX®–UF process shows much higher removal of DOC than that of coagulation, the rate of flux decline was greater. In addition, the rate of flux decline for the hydrophobic membrane was greater than for the hydrophilic membrane, regardless of pretreatment conditions used. When comparing coagulation with MIEX®', coagulation caused a lower rate of flux decline for both the hydrophilic and hydrophobic membranes due to enhanced formation of flocs. Furthermore, coagulation pretreatment reduced the fouling of the hydrophilic membrane, but did little to decrease the flux reduction of the hydrophobic membrane. Also, permeate flux declined with decreasing internal pore size, resulting from particle deposition into the membrane pore. This implies that all four fouling mechanisms are valid when applying these filtration models.

In addition, the experimental results prove that the MIEX® and coagulation pretreatment reduced the fouling of the membrane. Especially, the MIEX® + coagulation pretreatment process reduced membrane fouling. The results of analyzing in mechanisms on UF membrane fouling in applications of membrane materials and a coagulation pretreatment process showed that values of kinetic constants, K_s, K_i and K_c, were higher for the hydrophobic membrane than for the hydrophilic membrane. However, the kinetic constant K_c had a higher value for the hydrophilic membrane and the constants of K_s and K_i had higher values for the hydrophobic membrane. In the combination of coagulation with UF processes, flocs led to fouling due to cake layer formation on the surface of the hydrophilic membrane, while micro-flocs and membrane surface fouling led to fouling on the surface of the hydrophobic membrane. It was shown that the fouling on the surface was relatively lower but the fouling on the pore was relatively higher when the combination of MIEX and UF processes was employed.

In addition, values of kinetic constants, K_s, K_i and K_c, were relatively low in MIEX according to lower organic loading rates and larger flocs formed in the coagulation process when MIEX + coagulation + UF processes were employed. This observation suggests that much less fouling on the surface and pore on the membrane had made it quite less resistant for flux.

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