

다양한 지지체 분리막 위에 poly(vinyl alcohol)이 코팅된 나노복합막의 제조

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Preparation of poly(vinyl alcohol)-coated Composite Nanofiltration Membranes on Various Support Membranes

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요 약: Poly(vinyl alcohol) (PVA)이 폴리술폰 한외여과 막, 술폰화된 폴리에테르술폰, 폴리아미드 나노 막 위에 코팅된 나노 복합막을 가압법에 의해서 제조되었다. PVA는 글루타르알데하이드 수용액으로 가교되었다. 모든 지지층위에 PVA 희박용액이 성공적으로 코팅되어 나노복합막이 제조되었다. 지지막 위의 친수화도가 높아짐에 따라 수투과 유량이 증가하였다. 특히 음하전을 띠는 폴리아미드 나노 복합막의 제타전위는 PVA로 코팅함으로써 감소되었다. 막 오염 실험은 양이온을 띠는 계면활성제, 휴민산, 휴민산과 칼슘이온 복합체 및 bovine serum albumin을 사용하여 실행하였다. PVA로 코팅되지 않은 폴리아미드 나노복합막은 각각의 오염물질에 의해서 심하게 오염되었다. 휴민산과 단백질에 의한 오염은 오염물질의 등전점에서 가장 심하게 발생하였다. 휴민산에 이가 양이온을 첨가함으로써 오염이 심각하게 일어났다. PVA 수용액으로 폴리아미드 나노 복합막을 코팅함으로써 막 오염이 감소되었다. PVA로 코팅된 폴리아미드 나노 복합막은 산, 염기용액에 대해 저항성을 보였다.

Abstract: The poly(vinyl alcohol) (PVA)-based thin film composite nanofiltration (NF) membranes were prepared by coating polysulfone ultrafiltration membranes, sulfonated polyethersulfone and polyamide NF membranes with aqueous PVA solution by a pressurizing method. The PVA was cross-linked with aqueous glutaraldehyde solution. The NF membranes coated with a very low concentration of PVA on all the support membranes was successfully prepared. With increasing the hydrophilicity of the support membranes, the water flux increased. Especially, ζ -potential of negatively charged polyamide NF membrane was reduced by coating the membrane with PVA. A fouling experiment was carried out with positively charged surfactant, humic acid, complex of humic acid and calcium ion and bovine serum albumin. A non-coated polyamide NF membrane was significantly fouled by various foulants. The fouling process when using humic acid and protein occurred at the isoelectric point. There was severe fouling when using humic acid and adding bivalent cations. By coating the polyamide NF membrane with aqueous PVA solution, fouling was reduced. The polyamide NF membrane coated with PVA was resistant to the acidic and basic solution.

Keywords: nanofiltration, poly(vinyl alcohol), fouling, zeta potential, humic acid

1. Introduction

In recent years attention has been focused on the fouling of nanofiltration (NF) and reverse osmosis (RO)

membranes[1-3]. Vrijenhoek *et al.* reported that regardless of physical and chemical operating conditions, the rate and extent of colloidal fouling was most significantly influenced by the physical roughness of membrane surfaces. More particles deposit on rough mem-

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branes than on smooth ones[1]. Mntri *et al.* studied fouling behavior of different membranes differed by their cut-off values and their material properties, such as hydrophobicity. Adsorptive fouling was even more dramatic for the hydrophobic membranes. And high concentration polarization promotes fouling, which means that the rather loose NF membrane (NTR 7450) fouled more than the tighter NF membrane (Desal-5). Solution chemistry was also an important factor for membrane fouling[2]. Bouchard *et al.* studied humic acid adsorption onto the NF membranes coated with different materials. A polyamide NF membrane was less fouled than a cellulose acetate NF membrane[3].

A thin-film composite (TFC) polyamide membrane has been developed and commercialized due to its excellent membrane performance (high flux and rejection rate) for NF and RO[4]. However, polyamide can be easily degraded in the basic and chlorine solution. Therefore, in order to increase its stability, pretreatment like acid addition should be inserted in the process. In addition, TFC membranes, especially RO membranes are sensitive to fouling due to its very rough surface morphology. Many researchers were endeavored to enhance the flux by increasing the membrane surface area. In order to produce less fouling RO membranes, the membrane surface roughness should be reduced.

Most TFC membranes have negatively charged surfaces in the presence of water, which means that in the presence of positively charged solutes, the negatively charged membrane can be fouled heavily by the adsorption of counter-ionic solutes. In order to reduce the concentration of counter-ionic solutes near the membrane surface, the charge of membrane surface should be blocked by coating with neutral material such as poly(vinyl alcohol) (PVA) or soluble cellulose.

PVA is a chemically and physically stable material. Moreover, PVA may be attractive because of its hydrophilic and good film-forming properties. Because of its excellent properties PVA has been used for pervaporation[5] and RO membranes[6]. Lang *et al.* prepared TFC RO membrane with PVA and further cross-linking its surface[6]. Other researchers have also

tried PVA coating onto porous support membranes [7-10]. They used PVA of high concentration for TFC NF or RO membrane preparation in order to increase the separation property and decrease defect formations by a dip-coating method. The use of a high concentration of PVA may be one reason for its slower flux through the PVA membrane. With a low concentration of PVA it is not easy to prepare a high selective PVA membrane by the dip-coating method. In order to increase the membranes selectivity with a lower concentration of PVA, coating should be carried out several times. We used a new pressurized coating method instead of the dip-coating method to increase the stability of the coating layer.

In this study, we prepared and characterized NF membrane coated with PVA on hydrophobic polysulfone ultrafiltration (UF) membranes, hydrophilic membranes with sulfonated polyethersulfone and polyamide layer by a pressurized method. The fouling behavior was investigated by comparing a polyamide membrane with PVA-coated polyamide membranes with various foulants.

2. Experimental

2.1. Support Membranes

Polysulfone UF membrane (CSM-UF, SaeHan, Korea) with molecular weight cut-off (MWCO) of 50000 g/mol was used as a support for PVA-coating. Membranes of NTR-7410 (Sulfonated polyethersulfone, Nitto Denko, Japan) and CSM-NF (polyamide, SaeHan) were also employed as a support. The MWCOs of NTR-7410 and CSM-NF were 3000 and 400 g/mol, respectively.

2.2. Preparation of PVA-coated TFC Membrane

PVA of molecular weight of 35000~50000 g/mol (99% hydrolyzed) was supplied by Aldrich Chemicals (Milwaukee, WI). Aqueous PVA solutions of 0.001~2 wt% were prepared by dissolving PVA in 90°C deionized water for 5 hrs. The support membranes (CSM-UF, NTR-7410 and CSM-NF membranes) were

wetted in the PVA solution for 1min. The membrane was then pressurized and dried for 2 hr. The dried membrane was cross-linked by dipping into the glutaraldehyde solutions (GA, 25% aqueous solution, Tokyo Kasei Chemicals) for 30 sec. The GA solution was composed of H₂O/GA/HCl (87/10/3 wt%). The membranewas further cross-linked by drying at ambient temperature for 1 hr. The dried PVA membrane was wetted in 50 wt% aqueous ethanol solution.

2.3. Membrane Performance

The membranes were tested in a flow cell at 25°C and supported in the cell by a porous stainless steel disk. The test unit consisted of circular plate-and frame membrane cells, a back-pressure regulator and a high pressure pump (Hydracell pump, Model-13, Wanner Engineering, USA). The active area of the membranes was 17.35 cm². The membranes were compressed at 300 psi for 2 hr and then pure water flux was measured at 200 psi. The rejection rate was determined at room temperature and 200 psi using aqueous solution containing 1000 ppm of polyethylene glycol (PEG) 600 and 0.017 M of NaCl, CaCl₂, and Na₂SO₄.

2.4. ζ-potential Measurements

Surface ζ-potential of PVA-coated polyamide was measured by using a ζ-potentiometer (electrophoretic method, Otsuka Electronics Co.). The concentration of the electrolyte solution was 0.01 M NaCl at different pH values (3, 5.5 and 10).

2.5. Fouling Experiments

100 ppm of benzalkonium chloride (50% solution, cationic surfactant, Junsei) was used as a foulant. Other foulants were humic acid (Aldrich), complex of humic acid and calcium chloride and bovine serum albumin (BSA, Aldrich). Solution pH was controlled with NaOH and HCl. The concentration of humic acid and BSA was 100 ppm in water. The concentration of calcium chloride was in the range of 20~300 ppm. The tested membranes were CSM-NF and PVA-coated CSM-NF membranes. The initial water flux was fixed

to 1.5 m³/m²day. The flux was normalized by dividing flux with time (J) by initial water flux of steady state (J₀).

2.6. Durability of PVA-coated Polyamide NF Membrane

The durability of PVA-coated polyamide membranewas investigated by dipping for 7 days in 0.2 wt% solutions of citric acid and sodium hydroxide. The solution pHs of citric acid and sodium hydroxide were 4.0 and 10.0, respectively. The pure water flux and rejection rate of NaCl were compared.

3. Results and Discussion

3.1. Performance of PVA-coated NF Membranes

Various support membranes with different surface properties were coated with 0.05 wt% PVA aqueous solution in order to investigate the effect of the surface properties of the different support membranes on the performance of PVA-coated membranes. In general, PSf UF membranes have been widely used as a support for the preparation of thin film composite membranes by dip-coating and interfacial polymerization methods. The interaction of the ultrathin barrier layer with the surface of the underlying microporous support can affect the performance of the resulting membrane. In other words, a more hydrophilic support layer can collect permeate and conduct it to open pore. In order to confirm integrity of the PVA-coated membrane, coating should be repeated with high concentrated PVA solutions by a dip-coating method. At first, a PSf UF membrane was coated with aqueous PVA solution of different concentration (PVA/CSM-UF) in order to investigate the condition of the PVA coating and cross-linking by the pressurized method. In our new pressurized method one coating of PVA solution was enough to confirm the integrity of the resulting PVA membrane in contrast to the dip-coating method. Fig. 1 shows the performance of cross-linked and non-cross-linked PVA membranes on a hydrophobic PSf UF support membrane with concentration of PVA. GA was

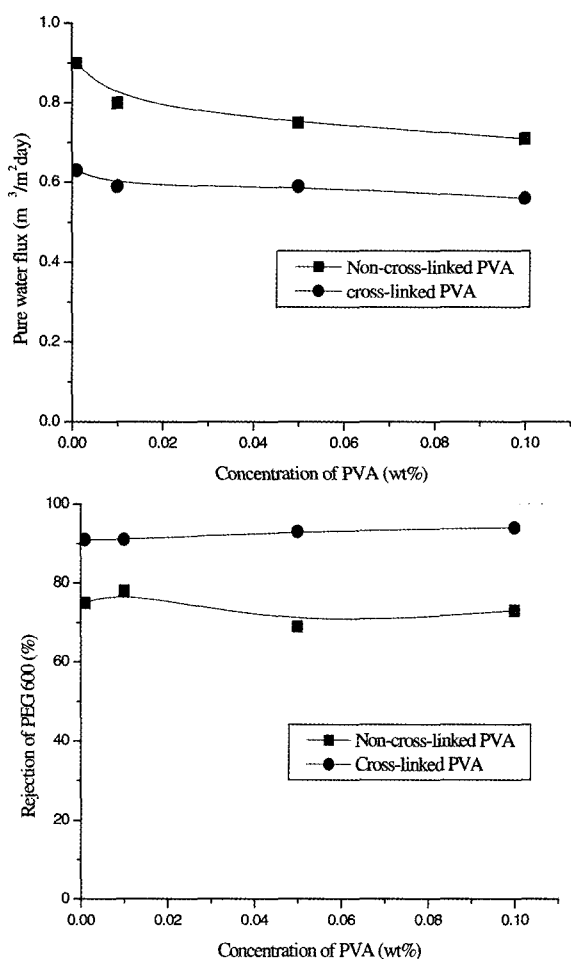


Fig. 1. Performance of cross-linked and non-cross-linked PVA membranes on PSf UF support membranes with concentration of PVA.

used for cross-linking the PVA. By cross-linking, the flux decreased and the rejection rate of PEG 600 increased. Surprisingly, even though very dilute PVA aqueous solution (0.001 wt%) was used, the rejection

rate of PEG 600 could be reached as much as 90%. However, the flux could not be enhanced enough. In order to increase the flux through the PVA membrane, the support membranes were changed to NTR-7410 and CSM-NF, which are more hydrophilic than PSf UF membrane (CSM-UF).

Table 1 shows the performance of the support and the PVA-coated membranes. As shown, with increasing the hydrophilicity of the support membrane the flux of the resulting PVA-coated membrane was enhanced without decreasing the rejection rate. When NTR-7410 with a sulfonated polyethersulfone-coated layer (PVA/NTR-7410) and CSM-NF with a polyamide-coated layer (PVA/CSM-NF) were used as a support, the flux of the resulting PVA-coated membranes could be moderately increased. The pure water permeation rates of PVA/NTR-7410 and PVA-CSM-NF are 1.2 and 1.8 m³/m²/day, respectively. These experimental results confirm that in order to enhance the performance of the PVA-coated membrane (high flux and rejection rate), more hydrophilic support membrane should be used. When harsh conditions (low or high pH) were applied to the membrane, the PVA/NTR-7410 membrane is better than the PVA/CSM-UF or PVA/CSM-NF membrane in terms of high flux and pH stability, respectively. The NTR-7410 and CSM-UF membranes have a better pH stability than the CSM-NF polyamide membrane. Moreover, the flux of the PVA/NTR-7410 membrane was higher than that of the PVA/CSM-UF membrane. However, when the membrane was used for water treatment, the PVA/CSM-NF membrane would be better

Table 1. Performance of Supports and PVA-coated Membranes

| | PWF (m ³ /m ² /day) ^a | Rejection rate (%) | | | |
|--------------|---|----------------------|-------------------|--------------------------------|--|
| | | PEG 600 ^b | NaCl ^c | CaCl ₂ ^c | Na ₂ SO ₄ ^c |
| CSM-UF | 8.36 | 0 | 0 | 0 | 0 |
| PVA/CSM-UF | 0.52 | 93 | 35 | 27 | 97 |
| NTR-7410 | 5.21 | 0 | 12 | 3 | 29 |
| PVA/NTR-7410 | 1.20 | 95 | 38 | 15 | 99 |
| CSM-NF | 1.93 | 99 | 52 | 37 | 99 |
| PVA/CSM-NF | 1.80 | 99 | 63 | 45 | 99 |

^{a-c}Tested at 200 psi; ^b1000 ppm of aqueous solution; ^c0.017 M of salt solution as an ionic strength

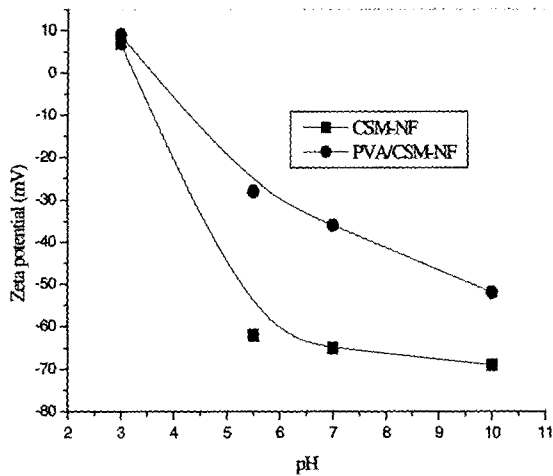


Fig. 2. ζ - potential curves as a function of pH.

in terms of high flux. Moreover, the PVA layer is more resistant to acids or bases than the polyamide layer. Acids or bases have been used for removing the fouled layer. In other words, without coating of polymeric material with high resistance to pH variation, the life time of polyamide NF membrane will be lessened by the attack of acids and bases.

3.2. Fouling by Cationic Surfactant

Generally, most of the NF or RO membranes have been made by interfacial polymerization. The surface of the membrane is negatively charged due to some hydrolysis of acyl halide groups to carboxylic acid groups. When the membranes are exposed to the solution of cationic solute, the membranes would be easily fouled by ionic interaction between membrane and cationic solute. Exposure to a cationic solute would cause a significant flux loss due to adsorption of the cationic solute. Therefore, the surface of the NF membrane should be neutral in charge in order to reduce the ionic attraction. Due to the PVA coating, the surface charge can be blocked. Fig. 2 shows the ζ -potential curves as a function of pH. As can be observed in Fig. 2, by one coating with a PVA aqueous solution, surface ζ -potential of the PVA/CSM-NF membrane was moderately reduced. At the conditions (pH 7.0) of the cationic surfactant fouling the membrane surface ζ -potentials were -67 mV and -40 mV for CSM-NF and

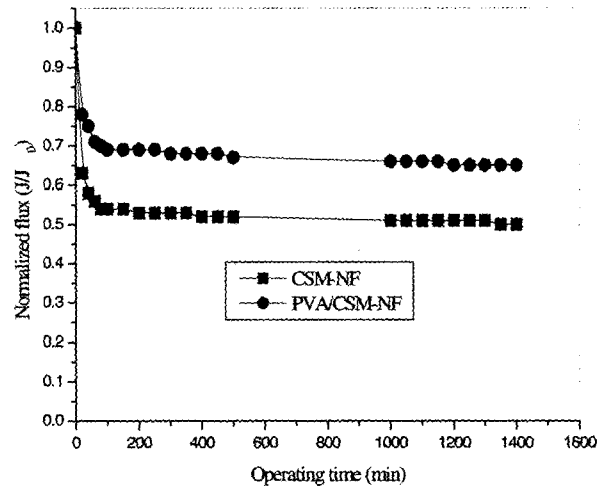


Fig. 3. Effect of cationic surfactant on fouling of CSM-NF and PVA/CSM-NF membranes: surfactant concentration, 100 ppm; pH 7.0.

PVA/CSM-NF membranes, respectively. These values indicate attractive electrostatic interactions between the positively charged cationic surfactants and the negatively charged membrane surface. It is further expected that attractive interactions are more significant for the more negatively charged membranes. Fig. 3 shows the normalized flux through a CSM-NF and a PVA/CSM-NF membrane when 100 ppm of cationic surfactant was nanofiltered at pH 7.0. The CSM-NF membrane was severely fouled as soon as cationic surfactant solution was contacted due to the attractive interactions between surfactant and membrane surface during the first filtration. In the case of PVA/CSM-NF membrane, flux reduction was not significant because of the reduced surface charge due to the PVA coating. In other words, when cationic solutes are filtered, commercialized polyamide NF or RO membranes are not suitable. The surface charge of polyamide membranes should be hindered by coating the membrane with neutral materials in charge such as PVA.

3.3. Fouling by Humic Acid

Humic acid has been used as a foulant[2,11-17]. Humic acid is charged at a higher pH than pH 3.5, which is isoelectric point (IEP). The humic acid is uncharged at the IEP. At higher pH, the humic macro-

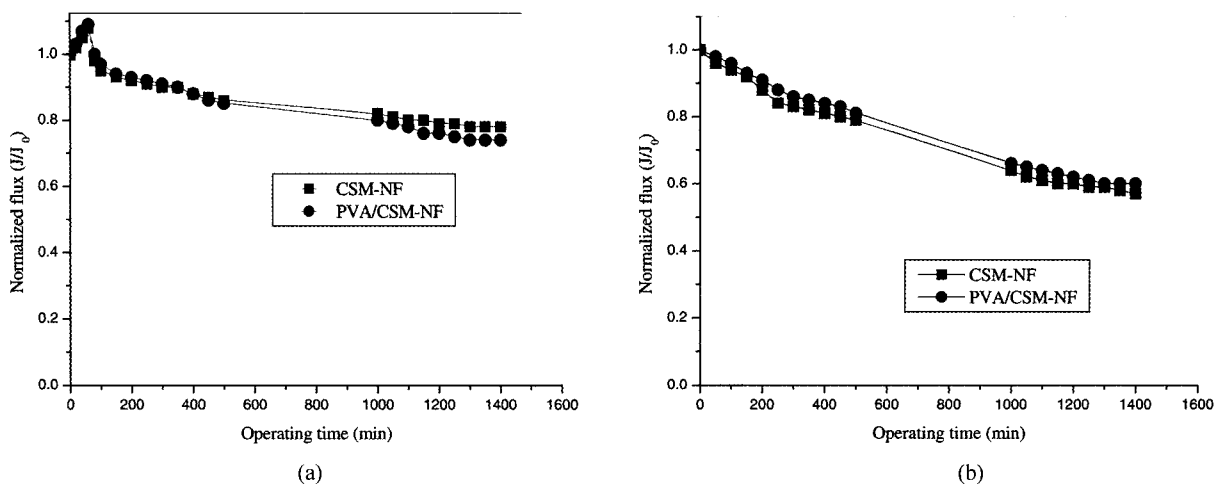


Fig. 4. Effect of solution pH on the fouling of CSM-NF and PVA/CSM-NF membranes: humic acid concentration, 100 ppm (a) pH 7.0; (b) pH 3.5.

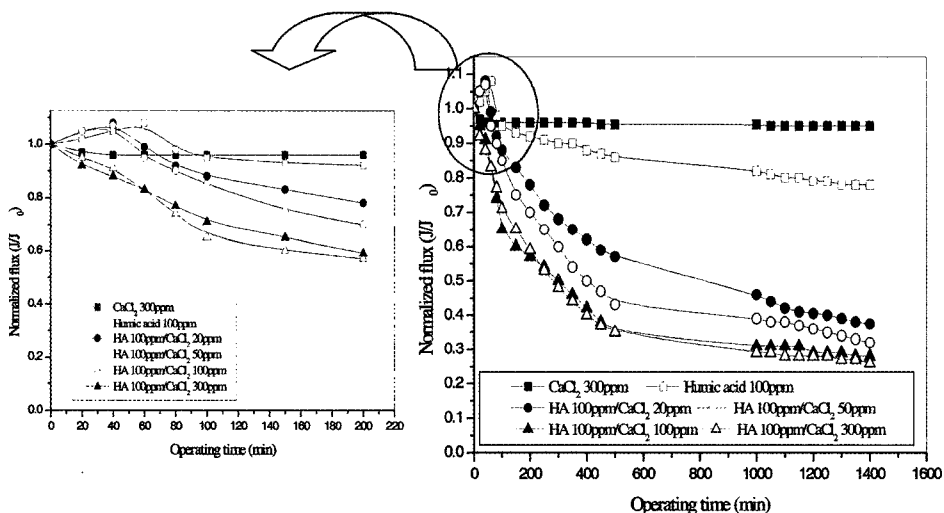


Fig. 5. Effect of calcium chloride concentration on the fouling of CSM-NF membrane: humic acid concentration, 100 ppm; pH 7.0.

molecules become extended and linear in shape due to the electrostatic repulsion. In contrast, at the IEP, the humic macromolecules become coiled and spherical in shape due to the interchain attraction. Fig. 4 shows the effect of pH on fouling of CSM-NF and PVA/CSM-NF membranes. At higher pH (pH 7), the membrane and the humic acid are negatively charged. Due to the electrostatic repulsion between membrane and humic acid, humic acid cannot easily adsorb on the polyamide NF membrane. By coating a CSM-NF polyamide membrane with PVA, the acidic group (-COOH)

is slightly shielded, as shown in ζ -potential data of Fig. 2. Due to the more positive charge of the PVA/CSM-NF membrane, the degree of fouling is greater than for the CSM-NF membrane. However, the flux reduction difference between these two membranes was not significant. During the filtration in the early period, the flux was increased because of the enhanced hydrophilicity as a result of humic acid adsorption. A similar trend has been reported by Mntri *et al.*[2]. However, further filtration of humic acid solution decreased the permeate flux due to the increased concen-

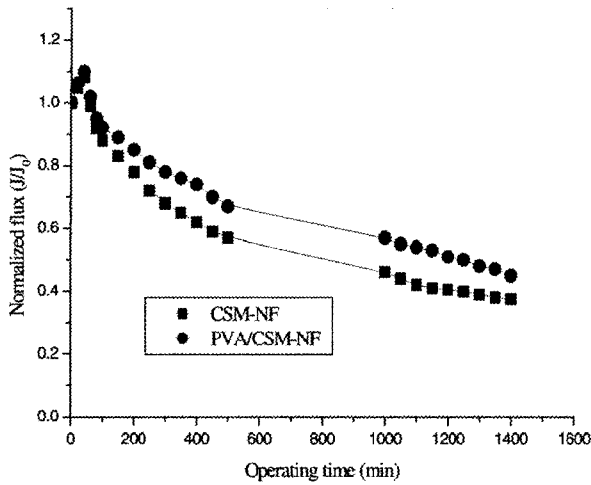


Fig. 6. Fouling comparison of PVA/CSM-NF with CSM-NF membranes: humic acid concentration 100 ppm; calcium chloride concentration 20 ppm; pH 7.0.

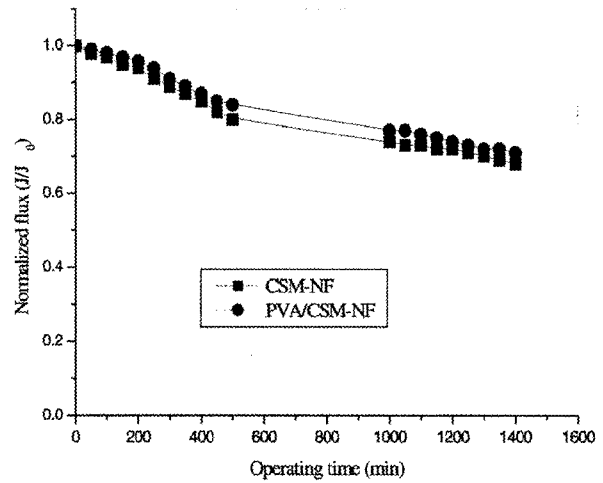


Fig. 8. Effect of BSA on the fouling of PVA/CSM-NF with CSM-NF membrane: BSA concentration 100 ppm; pH 4.6.

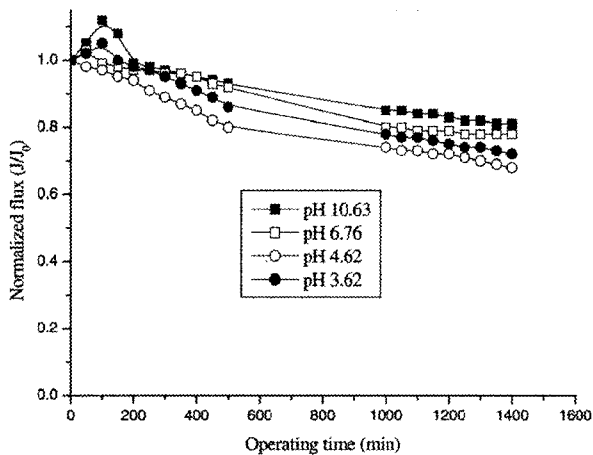


Fig. 7. BSA fouling behavior of CSM-NF membrane with pH.: BSA concentration 100 ppm.

tration polarization. Humic acid and calcium chloride alone was not significant foulants as shown in Fig. 5. Many researchers have shown that divalent cations such as Ca and Mg form complexes with the carboxylate groups of humic substances. As a result, the electrostatic repulsion of the humic acid molecule is decreasing. Moreover, also the electrostatic repulsion between the humic acid and the membranes is reduced. The hydrophilic parts (carboxylic acids) of the humic acid are shielded due to the complex formation. The increase in hydrophobicity of humic acid even increases the fouling of the membrane. In addition, the

hydrophilicity of the membrane would decrease due to the adsorption of divalent cations and the bridge of humic acid on the carboxylic acid of the polyamide membrane. By coating a CSM-NF membrane with PVA, carboxylic acid groups on the CSM-NF membrane are shielded. As a result, the effect of divalent cations on bridging between membrane and humic acid can be reduced. Fig. 5 shows the effect of calcium ion concentration on the CSM-NF membrane at pH 7.0. Normalized flux was rapidly decreased by the addition of a small amount of calcium chloride (20 and 50 ppm). Above 100 ppm of calcium chloride, fouling was occurred similarly. This may be due to the saturation of carboxylic acids of the CSM-NF membrane and humic acids by calcium ions. Moreover, a flux increase in the first 100 minutes of operation occurred up to a calcium chloride concentration of 50 ppm. However, a fast decrease in the flux occurred without the increase in flux during the first 100 minutes filtration by the addition of 100~300 ppm of calcium chloride. Fig. 6 shows the fouling comparison of CSM-NF and PVA/CSM-NF membranes by using 100 ppm humic acid solution added 20 ppm calcium chloride at pH 7.0. By coating CSM-NF membrane with PVA, fouling by humic acid complex was less than CSM-NF membrane. This can be explained by the

Table 2. Resistance to Acidic and Basic Solution of PVA/CSM-NF Membrane

| PWF (m ³ /m ² day) ^a | | | Rejection rate (%) of PEG 600 | | |
|---|--------------------------|-------------------|-------------------------------|--------------------------|-------------------|
| W/O ^b | Citric acid ^c | NaOH ^d | W/O ^b | Citric acid ^c | NaOH ^d |
| 1.8 | 1.6 | 1.6 | 63 | 62 | 63 |

^aTested at 200 psi; ^bBefore applying acidic or basic solution; ^c0.2 wt%, pH 4.0; ^d0.2 wt%, pH 10.0; dipping for 7 days.

reduced surface charge caused by the shielding of the carboxylic acid group shielding of the PVA/CSM-NF membrane.

3.4. Fouling by Protein

Amino acids and peptides which are amphiphilic can be separated in a pH gradient by NF membranes[18]. Moreover, conformation of peptides can be varied with pH. At the IEP, the peptides are coiled. The hydrophobic part of peptide is directed towards the solution. As a result, fouling can be significantly occurred by hydrophobic interaction between membrane and peptides. Fouling can be explained by ionic and hydrophobic interaction. A BSA solution has been used as a model solution for a foulant. The IEP of BSA is pH 4.62. At that pH, hydrophilic parts can be buried in the core. If the pH is higher or lower than the IEP, proteins are negatively and positively charged, respectively. Fig. 7 shows the fouling behavior of a CSM-NF membrane with pH of aqueous BSA solution. As can be seen, at the IEP the fouling of the membrane is higher than at another pH. At a higher pH (6.76 and 10.63) as the IEP, both protein and membrane are negatively charged. At a lower pH (3.62) as the IEP protein is positively charged and membrane is slightly positively or negatively charged. At the higher pH less fouling occurred caused by electrostatic repulsion between membrane and protein. Moreover, BSA is hydrophilic and extended in shape at these pHs. At the lower pH, the effect of electrostatic attraction on fouling is not significant. Moreover, the hydrophilicity of BSA is more important. At the IEP, although the CSM-NF membrane is negatively charged, fouling is more due to the hydrophobicity and coiled conformation

of BSA. In other words, the conformation of nano-filtered solute is very important. During the filtration in the early period, the flux was increased because of the enhanced electrostatic repulsion between membranes and BSA at the higher pH. However, further filtration of BSA solution decreased the permeate flux due to the increased concentration polarization. Fig. 8 shows the comparison of the fouling of the CSM-NF and PVA/CSM-NF membranes by BSA at the IEP, which is most sensitive to the membrane fouling. The PVA/CSM-NF membrane is less susceptible to the protein fouling than the CSM-NF membrane. This result shows that the surface material of the membrane significantly affects the protein fouling. From this fact it can be said that in order to protect the NF membrane against a solution containing foulant, the membranes should be coated with another material which is less sensitive to fouling. In our experiment of protein fouling, PVA was suitable as a coating material.

3.5. PVA/CSM-NF Membrane Durability

In general, a fouled layer can be removed by aqueous acidic (citric acid) and basic (sodium hydroxide) solution. In order to investigate the resistance of a coated PVA layer to acidic and basic cleaning solution, pure water and PEG 600 solution was nanofiltered with a PVA/CSM-NF membrane after applying a 0.2 wt% acidic and basic solution to the membrane. Table 2 shows that the performance was not changed after 7 days of dipping into the solution. In other words, a PVA-coated layer has a resistance to the cleaning solution, and a PVA layer has a higher durability than a polyamide layer in acidic and basic solution.

4. Conclusions

Various support membranes (hydrophobic (CSM-UF) and hydrophilic (NTR-7410 and CSM-NF) membranes) were coated with aqueous PVA solution by a pressurized method. Coating was successfully carried out and even very low concentrated PVA solutions (0.001 wt%) were used. When hydrophobic support membranes were

coated with PVA, the flux was very low. By using more hydrophilic support membranes (coating layer of sulfonated polyethersulfone and polyamide), the flux through the membrane became higher. When polyamide NF membranes were used as a support, the membrane performance was enhanced (slight flux decrease and rejection rate increase). All the membranes showed high rejection rate of PEG 600. The surface charge of the CSM-NF membrane was reduced by coating the membrane with PVA. A polyamide NF membrane was easily fouled by the cationic surfactant due to the electrostatic attraction. By coating CSM-NF membranes with aqueous PVA solution, fouling could be reduced. A polyamide NF membrane was fouled more by humic acid at the IEP due to the reduced electrostatic repulsion. PVA/CSM-NF membrane was fouled less by the humic acid at the IEP and the complex of the humic acid and calcium ion at pH 7.0 than CSM-NF polyamide membrane. When membranes were used with BSA protein solution at the IEP. Fouling was the most due to the hydrophobic interaction. By coating CSM-NF membrane with PVA, fouling was reduced. PVA/CSM-NF membranes were resistant to acidic and basic solutions, which were used for removing the fouled layer.

Acknowledgements

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