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Factors affecting the removal of isopropyl alcohol by reverse osmosis membranes for ultrapure water production

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ABSTRACT

Ultrapure water (UPW) is used in the electronic industry for the production of semiconductors, memories, and LCD displays. The two important pollutants for UPW production processes are ions and low-molecular weight (LMW) organic matters. To obtain UPW quality, several unit processes such as ion exchange, ultraviolet (UV) oxidization, and membrane filtration can be used together. Reverse osmosis (RO) which can remove LMW organic matters is one of the key treatment processes for UPW production. In this case, RO feed water contains very little materials such as ions, organic matters, and other pollutants. Thus, we investigated the factors affecting low-concentration LMW organic matter removal by RO membranes in deionized water to simulate the operation condition of RO process for UPW production system. Bench-scale experiments were carried out using four-inch RO elements from four different manufacturers. Isopropyl alcohol (IPA, molecular weight = 60.1) with concentrations less than 1 mg/l was used as a model LMW organic matter. The experimental results reveal that the possible mechanism for the IPA removal is steric hindrance of solutes by the pore structure of membrane. According to the mechanism, the IPA removal efficiency becomes higher at higher permeate flux and lower feed temperature, and RO membrane with higher salt rejection, and lower pure water permeability ensures the higher performance on the removal of IPA.

Keywords: Ultrapure water production; Reverse osmosis; Low-molecular weight organic matter; Isopropyl alcohol; Steric hindrance

1. Introduction

Ultrapure water (UPW) contains very little matters other than the water molecules in its body. UPW can be defined differently in terms of water quality parameters according to its end-users such as micro-electronics, pharmaceuticals, and supercritical boilers [1,2]. Thus it is characterized by a wide range of specific electrical resistances of 3–18 MΩ cm [3]. UPW production includes the controls of particles (bacteria, suspended solids), inorganic salts, and organic matters which are typically measured as the total organic carbon (TOC) concentration using the water treatment

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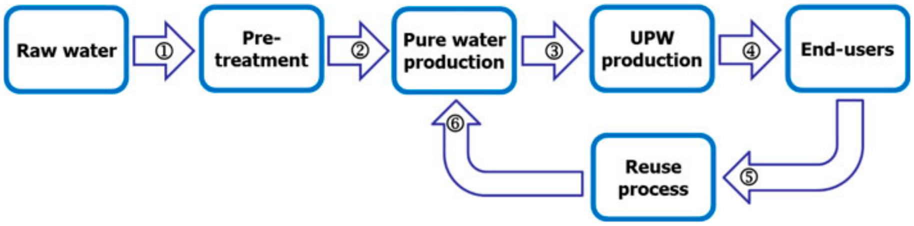
processes including reverse osmosis (RO), ion exchange (IX), and ultraviolet (UV) emission [4–9].

Fig. 1 shows the flow diagram and water quality of an example of UPW production system, which consists of pretreatment, pure water and UPW production, and reuse processes [10]. Pretreatment process is to remove the turbidity and particles using a combination of coagulation, media filter, activated carbon, disinfection, softener, and so on. Both turbidity and particles in the effluent (② in Fig. 1) of the pretreatment process are lesser than 0.5 and 1,000 to 10,000 count/ml, respectively. A small part of TOC may be removed due to the effect of coagulation.

The effluent of pretreatment enters pure water production process to remove ions, TOC, and remaining particles using a combination of RO, IX, degasifier, UV oxidation, and so forth. In this stage, the specific resistance becomes 10–15 MΩ cm (which is equivalent to 0.067–0.1 μS/cm in water conductivity) due to ion removal by RO and IX, while most of TOC is removed (③ in Fig. 1). The final stage is the UPW production process where the specific resistance and TOC become larger than 18 MΩ cm and lower than 5 μg/l (④ in Fig. 1) by a combination of IX, electrodialysis, UV emission, ultrafiltration, and so on. After the produced UPW is used (⑤ in Fig. 1), water quality becomes similar to that of the effluent of pretreatment, but TOC concentration is expected to be a little higher in the used UPW than in the effluent of pretreatment. Thus, the reuse process focuses on the removal of TOC using a combination of RO, activated carbon, UV oxidation or emission, IX, and so on. As discussed above, TOC is a very important parameter to control the performance of UPW production processes.

Conventional roles of RO process in UPW production are removals of ions and high molecular weight (MW) organic matters. RO process is generally positioned in the pure water production process (Fig. 1) and is composed of a two-pass system, where the permeate of the first-pass RO process is filtered by the second-pass RO membrane to increase water quality. When designing the two-pass RO system as a unit process for UPW production, a great concern is not on membrane fouling that is generally regarded as the most important factors in RO processes [11,12], but the low-molecular weight (LMW) organic removal.

If the second-pass RO process can remove LMW organic matters, the number of unit processes in UPW system may be decreased (e.g. the number of unit processes in UPW system is generally more than 20.), which means smaller cost of UPW production, easier maintenance and lesser risk for system failure. In this work, the second-pass RO process in UPW production system was considered in terms of LMW organic matter removal. The second-pass RO feed water contains very little materials such as ions, organic matters, and other pollutants. Thus, we investigated factors affecting low-concentration LMW organic matter removal by RO membranes in deionized water to simulate the operation condition of the second-pass RO process for UPW production system. Bench-scale experiments were carried out using four inches RO elements from four different manufacturers. Isopropyl alcohol (IPA, MW = 60.1) with concentrations less than 1 mg/l was



Water quality parameter	①	②	③	④	⑤	⑥
Conductivity [μS/cm]	100-200	100-200	-	-	10-500	1-20
Resistance [MΩ·cm]	-	-	10-15	>18	-	-
TOC [μg/L]	400-2,000	300-1,600	5-20	1-5	10-3,000	10-300
Turbidity [NTU]	1-20	<0.5	~0	~0	~0	~0
Particles [count/ml]	1×10^5-1×10^6	1×10^3-1×10^4	10-100	1-5	1×10^3-1×10^4	100-1,000

Fig. 1. An example of UPW production system targeting specific electrical resistance of water higher than 18 MΩ·cm and typical water quality parameters for each process.

used as a model LMW organic matter, which is frequently used as a representative TOC compound by RO membrane from Dow Filmtec, Woongjin Chemical, Toray and Nitto Denko.

The mechanism of organic matter removal by general RO processes were well known and the factors affecting the removal are as follows [13,14]: (1) MW and size, acid disassociation constant, hydrophobicity, hydrophilicity, and diffusion coefficient for organic matters; (2) MW cut-off, pore size, contact angle, and surface morphology for membrane characteristics; and (3) pH, ionic strength, and hardness for feed water composition. However, the operation of the second-pass RO process for UPW production system is limited to control the feed solution chemistry to enhance the organic matter removal efficiency. Adding chemicals to the RO feed should be prevented because the feed water characteristics are very close to deionized water with TOC in a very low concentration (μg/l level) and added chemicals to the clean feed water become new unwanted pollutants for the whole UPW production system. Thus, the organic removal mechanism related to solution chemistry is not important at all in the second-pass RO process for UPW production system. Therefore, the mass transfer parameters (flux, cross-flow rate, and solute diffusion) and membrane characteristics (pure water permeability and salt rejection) were considered as factors affecting the low concentration LMW organic matter removal in the second-pass RO process for the UPW system in this work.

2. Methods

2.1. Membranes and reagents

The commercial brackish water RO membrane elements from four manufactures (Dow Filmtec, USA; Woongjin Chemical, Korea; Nitto Denko, Japan; and Toray, Japan) were used in this work. The diameter of each element is four inches (10.16 cm). The characteristics of each element are listed in Table 1. In order to avoid any unexpected misunderstanding about the membrane characteristics on the removal of LMW organic matter, the title and company for each element are removed from the table.

The model LMW organic matter used in this study is IPA, which is frequently used to estimate the removal efficiency of TOC by commercial RO membranes. The molecular formula, specific gravity, and dynamic viscosity of IPA are C_3H_8O (MW = 60.1), 0.79 at 20℃, and 2.1×10^{-3} kg/sm at 25℃, respectively. The IPA with a desired concentration is dissolved in deionized water produced by a lab-scale water purifier, which consists of RO, IX, activated carbon, and media filter. The specific electrical resistance of the deionized water is guaranteed to be at least 10 MΩ cm.

2.2. Bench-scale RO test and analyses

Bench-scale RO tests were performed using a cross-flow RO system described in Fig. 2. Feed water enters into the feed channel in the RO element and are separated into permeate (through RO membrane) and concentrate (out of the feed channel). Then, both permeate and concentrate come out of the RO element and return to the feed tank to maintain the feed TOC at a constant value. A recirculating chiller is used to maintain a constant temperature in the feed tank.

At the start of each RO test, deionized water is filtered through the RO membrane to remove organic pollutants in the system (the inside of membrane element, pump, pipelines, pressure vessel, and so forth) until the TOC concentration in the concentrate reaches a value of less than 100 μg/l. After the cleaning process is finished, flux, concentrate flow rate (cross-flow rate), and temperature are set at the desired value for each experiment and the system is allowed to equilibrate up to several hours. Then, IPA of a desired concentration is spiked in the feed tank and the system is equilibrated until a constant TOC concentration

Table 1
The characteristics of RO elements provided by the manufactures

RO element	Membrane area (m^2)	Salt rejection (%)	Permeate flow rate (m^3/d)	Feed concentration (mg/l as NaCl)	Applied pressure (kPa)
A	7.9	99.0	8.5	2,000	1,500
B	7.9	98.5	9.5	1,500	1,050
C	8.7	99.7	11.0	2,000	1,500
D	8.7	99.2	9.5	2,000	830
E	7.9	99.6	7.2	1,500	1,050
F	8.0	99.0	7.6	500	760
G	8.0	99.0	7.2	500	700

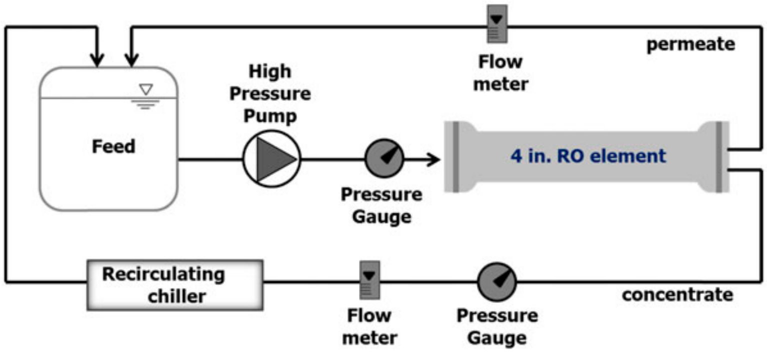


Fig. 2. Bench-scale RO test system.

in permeate is obtained. TOC is measured by Accura-R (T&C Technical, Japan), which is an online TOC analyzer with a range of 0.1–1,000 µg/l. Only a very low conductivity of sample (<1 µS/cm is allowed for this TOC analyzer), which is often used to measure TOC in a field of UPW production. After the TOC concentration of permeate reaches a constant value, the removal rate of IPA is determined by:

$$r = 1 - c_p/c_f \qquad (1)$$

where c_p and c_f are the permeate and feed TOC concentration.

3. Results and discussions

3.1. Suggested mechanisms for LMW organic matter removal

LMW organic matters can be removed by RO membrane according to one or more of the four mechanisms: (1) Pore size exclusion (Mechanism I) [13], (2) Solute diffusion across membrane (Mechanism II) [13], (3) Steric hindrance by pore structure (tortuosity and porosity) (Mechanism III) [13,14], and (4) the interfacial interaction between the solute and membrane (Mechanism IV) [15–17]. Pore size exclusion (Mechanism I) means that solutes larger than the pore size or MW cut-off of the RO membrane are excluded [13]. Solute diffusion across membrane (Mechanism II) means that the water mass transfer by convection dominates the solute mass transfer by diffusion, which is the general mechanism for ion rejection by the NF and RO membranes [13]. Steric hindrance by pore structure (Mechanism III) means that the solutes smaller than the pore size intrude the inside of the pore structure and they are stuck in the pore structure due to its tortuosity and porosity [13,14]. The interfacial interaction between solute and membrane (Mechanism IV) means that solutes can be repulsed or attracted by membrane surface and inner surface of the pore structures [15–17], which is beyond the scope of this work because the interfacial interactions are strongly dependent upon the solution chemistry. As discussed earlier, this work focused on the second-pass RO process for UPW production where the feed water property is very close to deionized water and it should not be controlled by adding chemicals. Thus, Mechanisms I, II, and III (Pore size exclusion, solute diffusion across membrane, and steric hindrance by pore structure) are considered in this study.

3.2. Effect of flux

Fig. 3 shows the effect of permeate flux on the IPA removal efficiency. As the permeate flux increased, the removal rate increased. If Mechanism I (pore size exclusion) is dominant, the IPA removal efficiency will be 100 % regardless of the permeate flux. Thus this mechanism should be excluded, which is reasonable because the MW of IPA is too small (MW = 60.1) to be

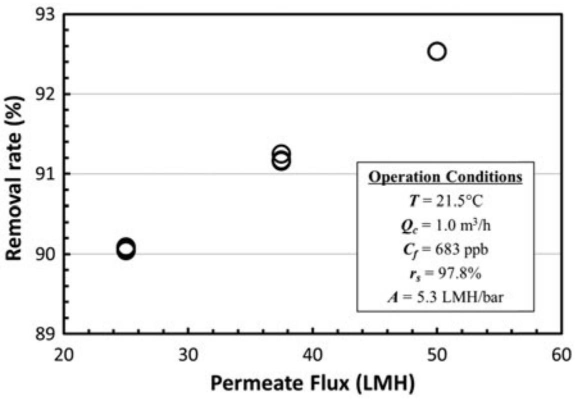


Fig. 3. Effect of flux on the removal of IPA.

completely rejected by the RO membrane. According to Mechanism II (Solute diffusion across membrane), the solute concentration in permeate decreases at higher flux because the water convection mass transfer increases at higher flux while the solute diffusion is not significantly changed due to the increase in permeate flux, which results in the higher removal rate at higher flux. According to Mechanism III (Steric hindrance by pore structure), the solute pass though RO membrane is not significantly affected by permeate flux because the solutes stuck in a complex pore structure are not easily removed by increasing water flow rate through RO membrane. Thus, Mechanisms II and III remain valid based on the results shown in Fig. 3.

3.3. Effect of feed temperature

Fig. 4 shows the effect of feed temperature on the IPA removal efficiency. Higher removal rate is observed at lower feed temperature, which can be easily explained by Mechanisms II (Solute diffusion across membrane) and III (Steric hindrance by pore structure) as in the case of the effect of flux on the IPA removal. As feed temperature decreases, the solute diffusivity decreases (related to Mechanism II) and the pore structure may be shrunken (related to Mechanism III), which results in the less salt passage at lower temperature. Still, Mechanisms II and III are appropriate to explain the IPA removal based on the results shown in Figs. 3 and 4.

3.4. Effects of feed TOC concentration and concentrate flow rate

Fig. 5 shows the effect of feed TOC concentration on the IPA removal efficiency. The feed TOC concentration affects the diffusion of solute through the membrane. As it increases, the solute mass transfer by diffusion also increases due to the increased solute concentration difference between feed and permeate sides, which results in higher solute concentration in permeate and lower removal efficiency at higher feed TOC concentration. However, the IPA removal efficiency was not significantly changed by feed TOC concentration. This result might suggest that Mechanism II (Solute diffusion across membrane) is not suitable to explain the IPA removal phenomenon.

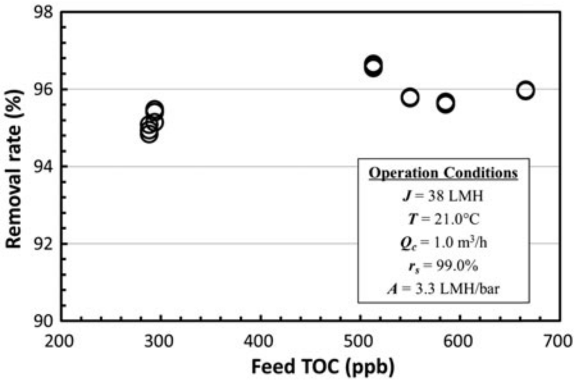


Fig. 5. Effect of feed TOC concentration on the removal of IPA.

Fig. 6 shows the effect of concentrate flow rate (cross-flow rate) on the IPA removal efficiency. The cross-flow rate affects the back-diffusive mass transfer of solutes away from the membrane surface [18,19]. As cross-flow rate increases, the back-diffusive mass transfer of solutes increases, which results in lower solute concentration on the membrane surface and higher removal efficiency at higher cross-flow rate. However, the IPA removal efficiency was not significantly changed by the concentrate flow rate. This will be another

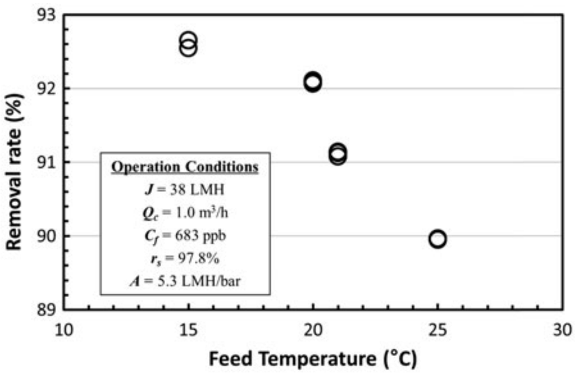


Fig. 4. Effect of feed temperature on the removal of IPA.

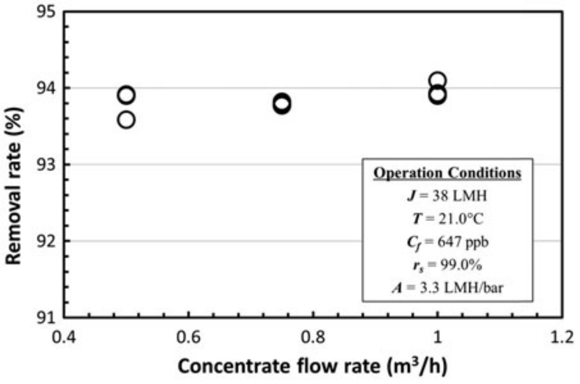


Fig. 6. Effect of concentrate flow rate on the removal of IPA.

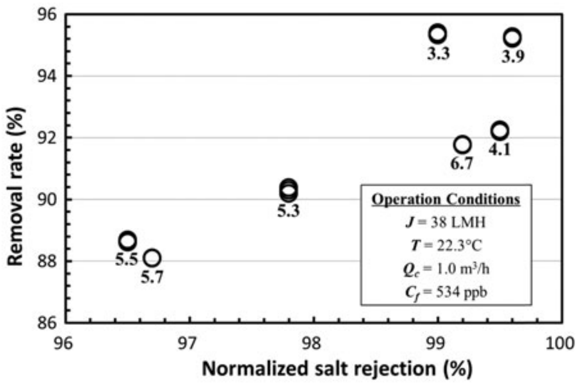


Fig. 7. Effect of membrane characteristics on the removal of IPA. Numbers under data points mean the pure water permeability in LMH/bar for the corresponding RO membrane.

reason why Mechanism II (Solute diffusion across membrane) is not appropriate to explain the IPA removal phenomenon.

3.5. Effect of RO membrane characteristics

Fig. 7 shows the effect of RO membrane characteristics on the IPA removal efficiency. The characteristics of RO membrane investigated in this work were the pure water permeability and salt rejection, whose data were obtained by the corresponding manufacture for each RO membrane. Since the operation conditions of tests by the manufactures are not identical, the salt rejection should be normalized using the method described elsewhere [12,20]. In Fig. 7, each number under the corresponding data point means the pure water permeability in LMH/bar for the corresponding RO membrane. Higher IPA removal efficiency is observed at higher salt rejection and lower pure water permeability, which can be explained by Mechanism III (Steric hindrance by pore structure). If an RO membrane has high salt rejection and low pure water permeability, its porosity and tortuosity are probably small and severe enough to prevent the solutes from passing through the membrane, which results in the high removal efficiency of the solutes. Therefore, it can be concluded that steric hindrance of solutes by pore structure (Mechanism III) dominates the IPA removal phenomenon by RO membrane.

4. Conclusions

It is advantageous in total cost, maintenance, and failure risk of UPW system, if RO membrane in the second pass of the two-pass RO process for UPW production effectively remove LMW organic matters because the number of total unit processes (generally larger than 20) can be decreased. Thus, this study focused on factors affecting the removal of low concentration LMW organic matters by RO membranes in deionized water, because the second-pass RO feed water contains very little materials including ions, organics, and other pollutants.

Bench-scale experiments using IPA as a model LMW organic matter and seven commercial RO membranes revealed that the main mechanism for the IPA removal was possibly steric hindrance of solutes by the pore structure of membrane. According to the mechanism, the IPA removal efficiency becomes higher at higher permeate flux and lower feed temperature, and RO membrane with higher salt rejection and lower pure water permeability ensures the higher performance on the removal of IPA. The new findings discussed above in this work suggest that the selections of high flux, low temperature, and RO membrane with high salt rejection and low pure water permeability will be able to enhance the removal efficiency of low concentration LMW organic matters by RO process for UPW production.

Acknowledgments

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