High flux ultrafiltration membrane for drinking water production

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Abstract The high flux ultrafiltration hollow fibre membrane (HFCA) for drinking water production was developed and the membrane performance was evaluated by long-term ultrafiltration testing with river water. The hollow fibre membrane was made of cellulose acetate (CA) and has a highly porous structure with a very thin dense layer on the internal surface of the membrane. The ultrafiltration flux of the HFCA membrane was compared with that of the conventional CA membrane without such a highly asymmetric structure. The flux for the HFCA membrane was almost twice as high as that for the conventional one. The performance of the conventional CA membrane was also compared with that of membranes with different materials, namely polyethersulfone (PES) and polyacrylonitrile (PAN). The result showed much higher flux for the CA membrane, indicating that the fouling can be effectively controlled by using the membrane with hydrophilic and negatively charged properties. It was shown that the high flux for the HFCA membrane was due to characteristics of both membrane material and porous membrane structure. The pilot plant testing was carried out to examine the performance in the long term operation, and confirmed the high performance of the HFCA membrane for the application of drinking water treatment.

Keywords Drinking water; high flux; ultrafiltration

Introduction

Membrane filtration using ultrafiltration (UF) and microfiltration (MF) membranes has become a much more popular process in drinking water treatment. Many large plants, which have a capacity larger than 10,000 m³/d, are being designed and constructed using this membrane filtration technology (Aldham et al., 1996; Morin, 1994). The increased use of the technology is due to several advantages of the membrane processes as compared to the conventional clarification, such as higher treated water quality, a more compact process, reduction in the amount of chemicals and easy maintenance (Clark and Tucker, 1993; Laine et al., 1991). One of the most attractive advantages is the extremely high removal of chlorine resisting pathogenic microorganisms such as Cryptosporidium and Giardia which are very difficult to remove sufficiently by conventional and filtration system (Dwyer et al., 1995). On the other hand, the treatment costs of membrane processes, which associated with the capacity, membrane facilities, raw water quality and so on (Adham et al., 1996; Wiesner, 1994) are still considered to be higher than the conventional treatment. In order to reduce the membrane treatment costs, increasing the permeate flux of the membrane filtration would be the most effective solution. However, membrane fouling prevents long-term stable operation with a high constant flux, because the increases in the flux tends to increase the filtration pressure more rapidly due to fouling and the frequency of chemical cleaning of the membrane.

Membrane fouling depends on several factors, such as membrane type, membrane system including feed pretreatment, operating conditions and raw water quality. Membrane material has a strong influence on fouling; i.e. the type of material determines the physicochemical interactions between the membrane and the substances in raw water, such as suspended inorganic particles, natural organic macromolecules (e.g., humic substances),
bacteria (Clark and Tucker, 1993; Laine et al., 1991; McDonogh et al., 1989). Most of these foulants can be removed from the membrane by hydraulic or pneumatic backwash, or air bubbling. Hence, in order to control the fouling and aim at a higher flux, selection of membrane type and washing method are particular important. Although various membrane types and washing systems have been developed to overcome the fouling problem and are used for drinking water production, innovation for novel high flux membrane is still desired.

In this paper, we introduce the high flux ultrafiltration hollow fibre (HFCA) membrane and show the filtration performance as compared with the conventional ultrafiltration membranes. The HFCA membrane is made of cellulose acetate (CA) and has a highly porous structure with a very thin dense layer at the lumen side of the hollow fibre membrane. In the previous paper (Nakasuka and Ase, 1995; Natatsuka et al., 1996) we showed that the flux for cellulose acetate ultrafiltration membrane (the conventional CA membrane) was much higher than that for the polyethersulfone (PES) membrane. The higher flux for the CA membrane is due to its highly hydrophilic property bringing less adsorption of foulant onto the membrane. In addition to the material characteristics of the CA membrane, the porous structure of the membrane is modified to be highly asymmetric near the internal surface. This paper describes the effects of both characteristics of the material and the porous structure of CA membrane on flux, in the system of inside-out cross-flow filtration with frequent backwash. The performance of the HFCA membrane is also examined in the pilot plant operation.

**Experimental**

**Source water**

The UF tests were conducted by using two source water qualities: the Ibo River downstream and the Sagami River in Japan. Table 1 shows the qualities of both raw water sources. The Ibo River water has a mean turbidity of 5.4 NTU and a mean total organic carbon (TOC) of 7 mg/L, and is rated as a relatively contaminated water source in Japan. The raw water was used as the feed water to the membrane system without pretreatment.

**Membranes**

The HFCA membrane is the cellulose acetate UF hollow fibre membrane with a nominal molecular weight cut-off (MWCO) of 150 kD. The membrane has very high porosity in the structure which results in very low membrane resistance ($R_m$) of $4 \times 10^{11}$ m$^{-1}$. For comparison, three types of hollow fibre membranes with different membrane materials were used; i.e. the conventional CA membrane, the polyethersulfone (PES) membrane and the polyacrylonitrile-polyvinylpyrrolidone copolymer (PAN) membrane with the MWCO of 150 kD, 30 kD and 100 kD respectively. These membranes have different MWCO but similar membrane resistance ($R_m$) of 10–14 $\times 10^{11}$ m$^{-1}$ and the same inside/outside fibre diame-

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Raw water quality</th>
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<tr>
<td></td>
<td>Ibo River</td>
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<tr>
<td>pH</td>
<td>6.6–8.1</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>2.4–77</td>
</tr>
<tr>
<td>Total iron (mg/l)</td>
<td>0.24–5.4</td>
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<tr>
<td>Total manganese (mg/l)</td>
<td>0.13–0.87</td>
</tr>
<tr>
<td>Total bacteria [1/ml]</td>
<td>500–4200</td>
</tr>
<tr>
<td>TOC (mg/l)</td>
<td>1.5–22.8</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>4.9–27</td>
</tr>
<tr>
<td>UV$_{250}$ (Abs/cm)</td>
<td>0.03–0.18</td>
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ter of 0.8/1.3 mm. All membranes used in this study were manufactured by Daicel Chemical Industries, Ltd. These membrane specifications and characteristics are shown in Table 2.

Ultrafiltration test apparatus and procedure

Figure 1 shows a schematic diagram of the bench-scale UF test apparatus. With this apparatus, four membrane modules with the effective membrane area of 0.5 m² can have their performances compared respectively with the same feed water quality. The system consists of two loops: a recirculation loop for cross-flow filtration and a loop for membrane backwash. The recirculation loop is comprised of a membrane module, a recirculation pump, a pre-filter with 200 µm mesh screen, a flow meter and two pressure gauges between inlet and outlet of the module. The raw water in a tank was initially introduced to the pressurised recycle loop in the system. The water was then prefiltered and delivered to the hollow fibre membrane module, in which the feed water passed through the lumen side of hollow fibres. A part of the water was filtered through the membrane as permeate, and the remaining water was recalculated as concentrate that was mixed with the feed water. The recirculation ratio (flow ratio of the recirculated water to the inlet feed water) was about 0.5. For bench-scale tests, the cross-flow UF were conducted at a constant transmembrane pressure of 50 kPa. The cross-flow velocity of feed water which passed through the lumen side of the hollow fibres was 0.15 m/s. Membrane backwash was performed periodically by pumping the permeated water from a permeate tank to the shell side of the hollow fibre membranes. The backwash was carried out for 1 min every 30 min. The water recovery was 90% for all test runs. The backwash water was injected with sodium hypochlorite at a concentration of 3 to 5 mg/L to inhibit the growth of bacteria on the membrane. After washing the foulant from the membrane, the water was discarded from the recirculation loop. The effective backwash pressure was 100 to 150 kPa.

For pilot plant testing, the large-sized membrane module with a membrane area of 50 m² is employed under the constant flux UF. The UF system is the same as that for the bench-scale test. The module has two permeate ports near both ends of the effective hollow fibre length of 0.9 m. In order to clean all the hollow fibres in the module uniformly, the backwashing was conducted in two steps; i.e. the backwash water was introduced from one permeate port for 30 s and the other port for the next 30 s. The backwash interval was 45 min and the water recovery was 90 to 92%.

Results and discussion

Characteristics of the membrane material

Table 2 shows the characteristics of the different membrane materials. The CA membrane has a relatively smaller contact angle measured by the sessile droplet method and a larger water sorptivity, which shows high hydrophilicity. Such hydrophilicity reflects lower adsorption of bovine serum albumin (BSA) to the CA membrane. In Figure 2, the UF fluxes

<table>
<thead>
<tr>
<th>Membranes</th>
<th>HFCA</th>
<th>Con. CA</th>
<th>PES</th>
<th>PAN</th>
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<tr>
<td>Membrane material</td>
<td>Cellulose acetate</td>
<td>Polyethersulfone</td>
<td>Polyacrylonitrile</td>
<td></td>
</tr>
<tr>
<td>MCWO (kD)</td>
<td>150</td>
<td>150</td>
<td>30</td>
<td>100</td>
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<tr>
<td>Rm (×10¹¹ m⁻¹)</td>
<td>4</td>
<td>14</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>Contact angle (deg)</td>
<td>50–55</td>
<td>65–70</td>
<td>52–58</td>
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<tr>
<td>Water swelling (g/g)</td>
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<td>0.4–0.6</td>
<td>2.5–3.6</td>
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<td>Adsorp. of BSA (mg/m², pH 5)</td>
<td>0.5</td>
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<td>1.3</td>
<td></td>
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<tr>
<td>Zeta potential (mV, pH 7)</td>
<td>–30</td>
<td>–4.2</td>
<td>–7.5</td>
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</table>
vs time for the conventional CA and the PAN membranes are compared. The fluxes are corrected to a temperature of 20 °C. The fluxes for both membranes decrease rapidly for 10 days after starting the filtration operation and reach nearly steady-state values. The flux for the CA membrane at the steady-state is almost twice as large as that for the PAN membrane. This indicates that the CA membrane is less fouled by the substances in the river water than the PAN membrane. Figure 3 shows the average UF fluxes for the conventional CA, the PES and the PAN membranes using two raw water sources. The average flux denotes the average value of the permeate fluxes at the steady-state region. For both raw water sources, the fluxes for the CA membrane are much higher than those for the PES and PAN membrane. The difference of the flux can be due to the difference of the material characteristics for the adsorption of the foulant to the membrane, because these membranes have similar $R_m$ and surface pore structure, which is observed by scanning electron microscope (SEM). The results indicate that the hydrophilic CA membrane has much more resistance to fouling than the other hydrophobic membranes and adsorbs small amounts of substances in the raw water. Such a low adsorption property in the CA membrane may not only be due to the high hydrophilicity, but also due to the highly negatively charged surface as shown in Table 2. The adsorption can be prevented by the electro-repulsion effect between the negatively charged membrane and the substance in river water, such as clay particles and humics, most of which are negatively charged.

**Characteristics of the membrane structure**

The UF flux can be increased by modifying the membrane structure even in the case of the same membrane material and the same pore size or MWCO. We have developed the novel CA hollow fibre membrane (HFCA) by increasing porosity of the dense layer near the internal surface of the membrane. The increase in the porosity brings about the increase in the pure water permeability or the decrease in the $R_m$. In Figure 4, the SEM pictures of the

![Figure 1 Schematic diagram of the UF experimental apparatus](image1)

![Figure 2 Comparison of flux profiles for the CA and the PAN membranes](image2)
cross-section of the HFCA membrane surface at the lumen side are compared with that of
the conventional CA membrane. The SEM shows the thin dense layer (skin layer) at the
internal surface of the hollow fibre and the relatively large porosity (dark part) near the skin
layer. Both cross-sections of the hollow fibre membranes consist of a three-dimensional
network-like part and a void part, and the thickness is 250 µm. The void part is positioned at
20 to 200 µm inside from the internal surface of the membrane. Figure 4 also shows the
porosity distributions of the cross-section of a three-dimensional network-like part from
the internal to the external surface of the membrane. It can be seen in the figure that the
porosity near the internal surface of the HFCA membrane is about four times larger than
that of the conventional CA membrane, indicating extremely low Rm and high water permeability for the HFCA membrane. In spite of the high porosity of the HFCA membrane,
the mechanical strength such as tensile strength and burst pressure of the membrane is the
same as that of the conventional CA membrane. In addition, both membranes have the same
MWCO of 150 kD.

Figure 5 shows the flux versus time for the HFCA membrane with R_m = 4×10^{11} \text{ m}^{-1} as
compared with the conventional CA membrane with R_m = 14×10^{11} \text{ m}^{-1}. It is obvious that
the fluxes for the HFCA membrane are almost twice as high as those for the conventional
CSA membrane and are maintaining a very high value of about 200 L/m²h. Such high flux
for the HFCA Membrane with low R_m may be due to the high washability of membrane
backwash. In order to see the relationship between the flux and the Rₘ, the variations of the fluxes with time are examined by using the membranes with the various Rₘ, as shown in Figure 6. Although the fluxes varied widely with time due to the variation of raw water quality, the higher fluxes were obtained for the membrane with the lower Rₘ. The fluxes for each Rₘ are averaged over time after 10 days operation: at steady state, and the average fluxes are plotted against the pure water permeabilities in Figure 7. The average flux increases linearly with the increase in the permeability. In the figure, the average fluxes for the PES membranes with different Rₘ are also shown. The increase in the average flux with the permeability for CA membrane is more significant than that for PES membrane, suggesting that the fouling for the hydrophilic membrane can be effectively controlled by the improvement of the membrane structure such as an increase in porosity. The filtration resistance due to the fouling can be calculated by using the following equation:

\[
J = \frac{P}{\mu} \left( Rₘ + R_f \right)
\]

where J is the average flux, \(\mu\) is the viscosity of water, P is the transmembrane pressure, and R_f is the resistance due to fouling. Figure 8 shows the R_f versus the Rₘ for the CA membranes. The PES membrane has a much larger R_f value of \(4 \times 10^{12} \text{ m}^{-1}\), suggesting that more intense fouling occurs for the membrane. The lower the Rₘ, the lower the R_f indicating that the fouling is controlled by reducing the Rₘ. It is generally said in the filtration without backwashing that the fouling is independent of the membrane resistance. In the filtration with backwashing, however, the reduction in Rₘ may allow the membrane backwash to be more enhanced because of increasing the flow rate of backwash water through the membrane.

**Figure 5** Comparison of flux profiles for the HFCA and the conventional CA membranes

![Figure 5](image)

**Figure 6** Comparison of flux profiles for the membranes with various membrane resistances, Rₘ

![Figure 6](image)
Pilot plant test using large-sized module

The pilot plant testing was carried out with the large-sized HFCA membrane module whose membrane area was 50 m². The testing was operated at a constant permeate flux of 90 L/m².h by controlling the transmembrane pressure. Figure 9 shows the results of transmembrane pressure corrected to temperature of 20 °C versus operating time. The variation of raw water turbidity and the water temperature are also shown in the Figure. The transmembrane pressure increased rapidly during 4 to 5 months operation, where the filtration resistance remarkably increased due to membrane fouling. However, during the testing period of about 10 months, chemical cleaning was cried out only once at 5 months, indicating that with the HFCA membrane stable operation can be conducted even in such a high flux design. The chemical cleaning which was performed with citric acid and sodium hypochlorite was very efficient and recovered the initial transmembrane pressure. Table 3 shows the permeated water quality and the raw water quality in this test. It was confirmed that the turbidity, total bacteria and total iron are perfectly removed by the membrane. However, the removal of organic compounds measured by COD and UV 260 was rather low. To increase the removal of such soluble organic and inorganic substances, the UF has to be combined with other treatments such as activated carbon treatment, ozonation, biological treatment, and nanofiltration. The effort will be made in future.
Conclusions

We have developed a novel high flux ultrafiltration hollow fibre (HFCA) membrane for drinking water production. The HFCA membrane is made of cellulose acetate (CA) and has a very porous structure with a very thin dense layer at the internal surface of the hollow fibre membrane. The UF flux for the HFCA membrane was almost twice as high as that for the conventional CA membrane, and 4 to 6 times higher than those for the polyethersulfone (PES) membrane and the polyacrylonitrile (PAN) membrane. The results indicate that the fouling can be effectively controlled by characteristics of both membrane material and porous membrane structure. The CA membrane has highly hydrophilic and negatively charged properties which control the adsorption of foulant to the membrane. The high porous structure around the internal surface of the HFCA membrane which provides lower \( R_m \) may allow the membrane backwash to be more enhanced. The pilot plant testing was carried out to examine the performance in the long term operation, and confirmed that stable high flux ultrafiltration was maintained using the large-sized HFCA membrane module.

References


Table 3 Raw water quality and permeated water quality

<table>
<thead>
<tr>
<th></th>
<th>Raw water</th>
<th>Permeated water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (NTU)</td>
<td>2.4–77</td>
<td>&lt;0.1</td>
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<td>Total iron (mg/l)</td>
<td>0.24–5.4</td>
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<td>Total manganese (mg/l)</td>
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<td>0</td>
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<td>TOC (mg/l)</td>
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<td>4.9–27</td>
<td>2.5–5.1</td>
</tr>
<tr>
<td>UV (_{260}) (Abs/cm)</td>
<td>0.03–0.18</td>
<td>0.02–0.068</td>
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