Behavior of micro-particles in monolith ceramic membrane filtration with pre-coagulation

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Abstract This paper is intended to clarify the characteristics unique to monolith ceramic membranes with pre-coagulation by referring to the behavior of micro-particles. Flow analysis and experiments have proved that monolith ceramic membranes show a unique flow pattern in the channels within the element, causing extremely rapid flocculation in the channel during dead-end filtration. It was assumed that charge-neutralized micro-particles concentrated near the membrane surface grow in size due to flocculation, and as a result, coarse micro-particles were taken up by the shearing force to flow out. As the dead end points of flow in all the channels are located near the end of the channels with higher filterability, most of the flocculated coarse particles are formed to a columnar cake intensively at the dead end point. Therefore cake layer forming on the membrane other than around the dead end point is alleviated. This behavior of particle flocculation and cake formation at the dead end point within the channels are unique characteristics of monolith ceramic membranes. This is why all monolith ceramic membrane water purification systems operating in Japan do not have pretreatment equipment for flocculation and sedimentation.

Keywords Coagulation; flow pattern; micro-particle; monolith ceramic membrane

Introduction

In the last decade, MF/UF membranes have been introduced in small to medium water purification plants to provide water purification with advanced particle removal functions, such as a safe barrier against Cryptosporidium. Recently, greater interest has been focused on pre-coagulation, which is intended to alleviate fouling, and to remove NOMs that cannot be removed even with UF membranes.

Looking back to the progress of membrane filtration, we see that, for economic reasons, research was initially done on the cross-flow filtration with higher membrane flux. Many research groups studied the limiting particle size removable through the lift effect produced by tangential flow and the relationship of the deposited particle size and its surface charge with specific cake resistance.

For water purification simple incidental facilities with less electricity consumption in the form of dead-end filtration should be utilized. Recent studies have dealt with the fouling of hollow fiber membranes by analyzing particle trajectories within the membrane. Also reported on were the advantages of adding pre-coagulation to the hollow fiber, which was achieved by providing flocculation and sedimentation, as in the case of existing rapid sand filtration processes. (Minegishi et al., 2001; Jang et al., 2002).

Many experiments and practical application in actual facilities have shown that water purification systems using the monolith ceramic membrane are stable for continuous six-hour dead-end filtration, even without addition of flocculation and sedimentation. This paper is intended to clarify the filtration characteristics of monolith ceramic membrane systems with pre-coagulation by analyzing the behavior of micro-particles.
Monolith ceramic membrane filtration systems

Recently in Japan, more than 300 water purification plants with MF/UF membranes have been operating and monolith ceramic membrane systems are incorporated in water purification plants. The water purification system with monolith ceramic membrane was developed in the early 1990s. After a demonstration in the MAC 21 project sponsored by the Ministry of Health and Welfare, this system has been introduced into water purification plants since 1996.

These monolith ceramic membrane systems initially employed a small membrane element with a diameter of 30 mm used in medical and food fields. This was subsequently replaced by a larger membrane element with a diameter of 180 mm to cope with the expected use in large size water purification plants. Specifications and filtration conditions are shown in Table 1. The filtration mode of monolith ceramic membranes is dead-end. Feed water is introduced in upward flow into a vertically set monolith ceramic membrane module from the bottom side. Washing waste is discharged downward normally through backwash with 500 kPa in a six-hour cycle. The actual plant operated with a chemical cleaning cycle of about 1 to 3 years.

At present, about 30 plants with a maximum capacity of 3,400 m³/day (1MGD) are in operation. Pre-coagulation has been provided to all of these plants to strengthen filtration performance and to reduce maintenance work, e.g. stable filtration for a maximum of several hundred units turbidity (Figure 1), enhancement of the removal of dissolved organic substances, alleviation of fouling, and reliable recoverability through chemical cleaning.

Consideration of theoretical models

Existing studies

The laminar flow model within dead-end hollow fiber membranes has been presented in many studies. For example, Fujita et al. (1994) developed the model below from the energy

Table 1 Specifications and conditions of ceramic membranes systems (1996–2002)

<table>
<thead>
<tr>
<th>Membrane element (Inside-out)</th>
<th>Size [mm]</th>
<th>φ30 × 1,000 L</th>
<th>φ180 × 1,000 L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane channel</td>
<td>I.D. 2.5 mm × 61</td>
<td>I.D. 2.5 mm × 2,000</td>
<td></td>
</tr>
<tr>
<td>Membrane area</td>
<td>0.48 m²</td>
<td>0.1 µm</td>
<td>0.1 µm</td>
</tr>
<tr>
<td>Nominal pore size</td>
<td></td>
<td>40–45 m³/m²/day</td>
<td>40–45 m³/m²/day</td>
</tr>
<tr>
<td>* at 100 kPa, 25°C Specific flux*</td>
<td>25–30 m³/m²/day</td>
<td>150 m³/m² (max)</td>
<td></td>
</tr>
<tr>
<td>Module</td>
<td>Membrane area</td>
<td>73 m² (max)</td>
<td>150 m² (max)</td>
</tr>
<tr>
<td>Filtration conditions (Dead End Mode)</td>
<td>Operating design flux</td>
<td>1–2 m³/m²/day</td>
<td>1.5–2.5 m³/m²/day</td>
</tr>
<tr>
<td></td>
<td>Filtration duration</td>
<td>6–12 hours</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Backwashing Pressure</td>
<td>500 kPa</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water recovery rate</td>
<td>&gt;98.5%</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1 Example of TMP vs. turbidity of raw water
equation and the material balance in the course of filtration:

\[
\frac{dp}{dv} = -\frac{v}{g} \left[ 1 - \frac{8 \cdot \mu}{\rho \cdot d \cdot k \cdot (p - p_o)} \right] \tag{1}
\]

where \( p \) = static pressure (m), \( v \) = axial velocity within the hollow fiber (m/s), \( g \) = gravitational acceleration (m/s\(^2\)), \( \mu \) = viscosity (kg/m/s), \( \rho \) = water density (kg/m\(^3\)), \( d \) = inside diameter of the hollow fiber (m), \( k \) = membrane filterability (s\(^{-1}\)), and \( p_o \) = external pressure of the membrane (m).

Considering the characteristic values \( (d = 4 \times 10^{-4}, k = 6 \times 10^{-6}) \) of the hollow fiber, the first term on the right side of Eq. (1) is smaller than the second term. So neglecting the first term, axial velocity \( v \) was derived by applying the boundary conditions to this equation:

\[
v = \beta \cdot (p_f - p_o) \left[ \tanh(\alpha \cdot L) \cosh\left\{ \alpha \cdot (x - L) \right\} + \sinh\left\{ \alpha \cdot (x - L) \right\} \right] \tag{2}
\]

where \( p_f \) is the pressure at the inlet of the hollow fiber, and

\[
\beta^2 = \frac{\rho \cdot g \cdot d \cdot k}{8 \mu}, \quad \alpha = \frac{4 \cdot d \cdot k}{d^2 \cdot \beta} \tag{3}
\]

In the laminar flow of an inside-out type MF/UF membranes, particles larger than 0.1 \( \mu \)m are governed by shear induced motion, and the critical particle size related to deposition on the membrane surface is likely to be in the range of 10–50 \( \mu \)m (Wiesner et al., 1992). Recently, it was pointed out from the trajectories theory and the experimental results in reference to the dead-end hollow fiber membrane that, when the particle size increases, a decrease in axial velocity within the membrane causes deposition of particles on the membrane surface, resulting in clogging at the membrane end. On the basis of this result, it was proposed that clogging could be avoided by operating in the semi-dead end mode in which the concentrate is discharged from the hollow fiber membrane end (Panglish, 2002).

It was confirmed that membrane filterability with pre-coating coagulant was worse than that of ordinary or in-line coagulation conditions (Park et al., 2002). A study was also done on promoting floculation by using turbulence in the water pipe systems to the membrane unit after addition of coagulant (Hagmeyer et al., 2003). These studies indicate the importance of the way in which the coagulant acts on the membrane surface when pre-coagulation is to be combined with the membrane. However, no study has yet been done on floculation accompanied with concentration near the membrane surface as in the case of monolith ceramic membranes.

**Proposed model for monolith ceramic membrane**

The analysis value of hollow fiber membranes according to the Eq. (2) above is practically equal to the value calculated numerically from Eq. (1) using Secant and Runge-Kutta methods. At the case of monolith ceramic membranes \( (d = 2.5 \times 10^{-3}, k = 5 \times 10^{-5}) \), however, the difference between analysis and numerical calculation values is 15% or more, which means that Eq. (2) cannot be applied. In order to enable the analysis of Eq. (1), a new equation is developed.

Without ignoring the first term on the right side of Eq. (1), the following approximate velocity solution could be obtained:

\[
v = v_f \cdot \cosh(\alpha \cdot x) - \frac{\beta \cdot (p_f - p_o)}{2g} \cdot \frac{v_f^2}{2g} \cdot \sinh(\alpha \cdot x) \tag{4}
\]

where \( v_f \) = inlet velocity (m/s). Note that energy and material balance equations are omitted here. Eq. (4) appears to represent correctly the axial velocity in the monolith channels, and
provides an expanded approximate solution including hollow fiber membranes for larger $d$ and $k$.

On the other hand, monolith ceramic membranes have a channel structure in the membrane element, so that each channel filterability $k$ has a certain distribution. To facilitate analysis of the flow pattern on the basis of this distribution, a five-channel model with three levels of filterability was assumed as shown in Figure 2. These were selected to represent the filterability distribution of an actual membrane element more simply.

Solving the equation Eq. (4) by providing appropriate material balance and boundary conditions, the velocity equation of the five-channel model can be solved as follows:

$$v_i = v_{fi} \cdot \cosh(\alpha_i \cdot x) - \beta_i \cdot (\bar{p}_{fi} - p_e) \cdot \sinh(\alpha_i \cdot x) \quad (i = 0, 1, 2)$$

where $\bar{p}_{fi}$ is the total pressure at the channel inlet, $p_e$ is the external static pressure of the membrane (m). The flow pattern in monolith ceramic membrane module is shown in Figure 3. A concentrate flowing out through outlets of channels 1 and 2 with lower filterability is drawn into channel 0 with higher filterability. It was also confirmed that the dead end point is located at the position with an axial velocity $v_j = 0$ in channel 0.

The axial velocity $v$ determined from Eq. (5) are shown in Figure 4 for a membrane flux of 2 m$^3$/m$^2$/day. On the basis of these results, the water recovery in channels 1 and 2 with low filterability was calculated to be 96.5%, and 90%. The average $G$-value in the channels is calculated about 40 s$^{-1}$, which is included in the optimum flocculation conditions pointed out by Camp et al. (1943). On the other hand, the hydraulic residence time in the channel is about 50 seconds, which is evidently too short for flocculation. Actual flocculation effects are described in subsequent sections.

**Experimental consideration**

**Experiments using ceramic membrane system with pre-coagulation**

The particle size distributions were studied in each portion of the system to clarify the characteristics of the monolith ceramic membrane with pre-coagulation. Figure 5 shows the experimental set-up and sampling points. The raw water was taken from the Kiso River. The dosage of coagulant was set at 1 mg-AI/L. The coagulant was mixed under the condition of $G$-value of 150 sec$^{-1}$ for five minutes. Two membrane modules as shown in Table 1 were used. Pre-coagulated water was introduced upward from the bottom of the module. The feed rate was controlled at the membrane flux of 2 m$^3$/m$^2$/day.

**Visual experiment on floc (with small and large membrane modules)**

The top and bottom portions of the module casing were designed by transparent parts to enable a visual check of the floc condition at both membrane modules. The floc condition was observed during filtration (6 hours), and recorded with a video recorder.
Measurement of particle size distribution (with small membrane module)

The particle size distribution was measured at the four points (SP-1 to SP-4) as shown in Figure 5, by using the batch type cell holder (Horiba LY-073) with the laser diffraction scattering type particle size distribution measurement system (Horiba LA-700).

Measurements of critical particle size (with small membrane module)

The behavior of 0.5–15 μm particles within the lower filterability channels was also measured. The filtration flux was set at 2 m³/m²/day, and the outflow rate from the top was controlled to obtain the outlet flow of channels 1 and 2, as shown in Figure 4 (recovery ratios 96.5% and 90%). Polystyrene type latex particles (JSR Stadex/Dynospheres: 0.5, 3, 5, 10, 15 μm, specific weight 1.05) with uniform size were used. To eliminate the effects of aggregation, an extremely small amount of dispersant was added into the feed water.

Experimental result

Visual experiment

There was no constantly visible floc in the lower portion of the membrane where coagulated water entered. On the other hand, we observed that visible flocs blew out at a rate of 3–8 mm/s from the inside channels in the upper portion of the membrane. The floc amount was evidently greater there than in the lower portion. The blown-out floc particles indicated that the flow line formed an arc from the center toward the periphery, and that most of them were sucked into the peripheral channels.

In the course of the initial one to two hours of the total filtration time of six hours, a
blanket of floc particles appeared, then grew in the upper inside part of the membrane.

When backwashing was started after the stop of filtration, this blanket was sucked instantaneously into the channel group, and simultaneously, the columnar cake was pushed upward from the channel near the periphery. Later on, the compressed air from the module top caused water, floc particles, and cake to be sucked entirely into the channels and discharged from the module bottom.

**Measurement of particle size distribution**

The results of the measurement of particle size distribution of SP-1 to SP-4 are shown in Figure 6. The particle size of the raw water (SP-1) was smaller than 15 µm. The SP-2 obtained after the mixing tank indicated a peak at 60 µm. In the case of SP-3 at the inlet of the membrane after shearing in the pump, floc particles were disaggregated with a peak at 8–9 µm. On the other hand, samples in the membrane upper portion (SP-4) indicated that the distribution had peaked at 70 µm, which indicates concordance with the observation result of the visual experiment.

**Measurements of critical particle size**

We compared the micro-particle number in the membrane lower inlet with the number in the upper outlet under flow conditions for channels 1 and 2 in Figure 4. The result showed an almost similar micro-particle concentration at both flow points using latex particles (0.5–15 µm).

**Discussion**

**Flow pattern in monolith ceramic membrane module**

In order to verify the flow pattern model, the outflow rate at the membrane top and the position of the dead end point were compared with experimental results. From the analytical result with the 5-channel model, the outflow rate at the membrane top was estimated to be 2–4 mm/s as shown in Figure 4. On the basis that the maximum flow velocity in laminar flow is twice the average, the 3–8 mm/s value confirmed in the visual experiment corresponds well with the model predicted value. In addition, the actual caking position matches acceptably well with the dead end point predicted by the model analysis. These results demonstrated that the 5 channel model is substantially representative of the flow phenomena of actual monolith membranes.

**Re-aggregation of disaggregated flocculation particles**

This experiment proved that coagulated floc particles were disaggregated in the subsequent
pump. As these disaggregated particles were already charge-neutralized, re-coagulation can be achieved if contact opportunity and reaction time are properly provided for coagulation of micro-particles.

The experimental result on critical particle size with latex indicates that, at least, spherical particles of smaller than 15 µm are deposited onto the membrane surface in the course of membrane filtration. On the other hand, the measurement result shown in Figure 6 indicates that particles entering the membrane were disaggregated flocs with a size of smaller than 15 µm. And the visual experiment confirmed that a large amount of coarse flocs flew from the membrane. These results show that particles once carried near the membrane surface were released from the membrane surface in the course of filtration.

Next, we considered the flocculation phenomenon near the membrane surface within a thickness of one or two hundred micrometres. The flow condition of this zone can be calculated by Eq. (5) and laminar flow equation. From these calculated results, the average of the linear velocity is about 500 µm/s, so the residence time distribution is supposed to reach some ten minutes to some hours. This is long enough for flocculation. The shear rate \( G \) is distributed from 100 to 20 s\(^{-1}\) in the channel length. These are desirable shear conditions pointed out by Camp.

As shown in Figure 7, the charge neutralized particles carried into the channels are concentrated near the membrane surface by membrane filtration, and grow into large aggregates by flocculation.

Micro-particles, larger than 1 µm studied here in the shear field, are subject to a lift stress such as lateral migration, and shear-enhanced diffusion, proportional to the square or cubic of the particle equivalent diameter \( d_p \) (Cohen et al., 1986). Then, the flocculated particle is lifted up by laminar flow and carried out from the end of the channels. Therefore, the space near the ceramic membrane surface might be considered to be a high efficient field for coagulation of charge-neutralized micro-particles.

**Distribution of solids in the module**

Figure 8 shows the result of a survey on the distribution of solids in the large membrane module after six hours filtration. Solid cakes, hollow cakes, the blanket layer, and the amount of sediments in the piping below the module were actually measured, and the amount of cake layer on the membrane in places other than the dead end point was estimated from the balance of water quality analytical data. Solid cakes are columnar compacted cakes, which retain their shape even after backwashing discharge. Hollow cakes are cakes previous to the solid cakes and have a cavity around their central axis, so that they are disaggregated into particles or flocs during backwashing.

Generally, operation of the inside-out type membrane in dead-end filtration is associated with deposition of the entire amount of inflow solids onto the membrane surface, resulting in rise of the trans-membrane pressure within a short period. In the case of a monolith ceramic membrane, most of the inflow solids were caked at the dead end point of the channels with high filterability, as shown in Figure 8. They formed a floc blanket layer in
the upper portion of the membrane. Therefore, the solids loading on the membrane surface other than around the dead end point can be reduced to about 25% of the total inflow solids.

These features of monolith ceramic membranes with pre-coagulation are considered as useful for allowing six-hour continuous filtration without providing pre-treatment processes, such as flocculation and sedimentation, even when the raw water is highly turbid. Note that the actual equipment incorporates a control, which monitors the trans-membrane pressure in every filtration cycle and overrides the set filtration time to activate backwashing when the pressure difference reaches a range from 30 to 50 kPa.

**Conclusion**

Flow analysis and filtration experiments confirm that the monolith ceramic membrane module in dead-end mode has a unique flow pattern. After charge neutralization and aggregation through pre-coagulation, micro-particles disaggregated in the pump were increased in size rapidly to become coarse for discharge in spite of short hydraulic residence time in the monolith membrane. This phenomenon is presumed to have been caused by micro-particles flowing into the membrane element, and then increasing in size through aggregation in the course of concentration near the membrane surface, followed by back diffusion from the membrane surface into the bulk flow by the shear-induced lift force. Flocs flowing out from the channels with low filterability were caked at the dead end points of the channels with high filterability. Some of these flocs were detained in the form of blanket in the upper part of the membrane. When the ceramic membrane is to be combined with pre-coagulation, flocculation is not necessary to perform because the monolith membrane itself has characteristics that promote re-aggregation. In addition, sedimentation is usually not necessary because the solids loading acting on the ceramic membrane is divided into the cake formed intensively at the dead end point and the blanket detained in the upper portion of the membrane. Therefore, all monolith ceramic membrane water purification systems currently operating in Japan do not use the two pretreatment processes of flocculation and sedimentation.

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References