Virus removal by ceramic membrane microfiltration with coagulation pretreatment


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Abstract The performance and mechanism of virus removal by microfiltration with coagulation pretreatment were investigated. We confirmed the unexpectedly high performance of virus removal for two types of ceramic membrane system: a positive pressure-driven dead-end filtration with inside-out configuration and a vacuum pressure-driven dead-end immersed filtration with outside-in configuration. Virus removals by both systems were more than 7 logs, although the size of the tested Qβ virus (23 nm) was much smaller than the membrane nominal pore size of 100 nm. The virus inactivation by the addition of the coagulant (PACl) and the virus adsorption onto the floc retained on the membrane surface mainly contributed the virus removal. No virus accumulation in the retentate was observed, possibly due to the virus inactivation by the coagulant.

Keywords Ceramic membrane; coagulation; microfiltration; virus

Introduction

The addition of coagulants to the feed water of the membrane unit in the treatment of surface water is beneficial for ceramic microfiltration (MF) and sometimes also beneficial for polymeric MF and ultrafiltration (UF). Coagulation pretreatment alleviates the decline in permeability, and thereby reduces the frequency of hydrodynamic- or chemical-cleaning procedures used to maintain permeate flux. It is also beneficial for filtrate quality, as some dissolved contaminants, which are small enough to pass through the membrane, are aggregated by the coagulant and are thereby effectively removed in the membrane separation process. For the removal of viruses, however, the effect of coagulation pretreatment and its mechanism have not yet been fully investigated.

Although UF can achieve more than 6 log (99.9999%) virus removal, MF cannot efficiently remove viruses when the filtration mechanism relies on physical sieving alone. The viruses of concern in water are small enough to pass through the pores of MF membranes – the lower limit of the pore diameter in MF membranes is approximately 0.1 µm. Nonetheless, it has been observed that MF membranes remove viruses at a better than expected rate. Kolega et al. (1991) tested a hollow-fiber polypropylene membrane (0.2-µm pore size, Memcor® continuous microfiltration system) by treating secondary effluent from a sewage treatment plant, and reported a 2- to 6-log reduction of human enteroviruses. Coffey et al. (1993) conducted an experiment using surface water seeded with a bacterial virus, MS2, and reported between 1.7- and 2.9-log removal of MS2 with a hollow-fiber microfiltration membrane with a 0.2-µm pore size, which is 10 times larger than the size of MS2 (0.02 µm). In addition to the physical sieving, two phenomena appear to relate to and contribute to virus removal: the formation of the cake layer on the membrane surface and hydrodynamically irreversible membrane fouling (Jacangelo et al., 1995). The cake layer that forms as a result of coagulation pretreatment is advantageous for virus removal – some viruses have a tendency to adsorb onto the aluminum floc particles (e.g., Clesceri et al., 1998), which are finally retained by the membrane to form the cake layer. Although
coagulation pretreatment also reduces the irreversible membrane fouling that may also be beneficial for virus removal, a recent finding that aluminum coagulation inactivates viruses (Matsui et al., 2001) is another advantage of coagulation pretreatment.

The objective of the present study is to investigate the performance and the mechanism of virus removal by MF with coagulation pretreatment. We confirmed the unexpectedly high virus removal performance of both pressure-fed and immersed ceramic MF systems.

Materials and methods

Coagulation-MF systems

Polyaluminum chloride (PACl, 10% Al₂O₃, 62.5% basicity, Sumitomo Chemical Co. Ltd., Tokyo) was used for coagulation pretreatment. Two types of ceramic membrane filtration systems were investigated. Figure 1 shows the schematic diagram of the pressure-fed ceramic MF and the coagulation pretreatment system. The system with a monolith ceramic module (multi-channel tubular, nominal pore size of 0.1 µm) in a casing was operated in a dead-end mode. The flow of feed takes place at a constant rate inside of the module by positive pressure. Two types of coagulation operation were investigated: a conventional mechanically stirred mixer and a static mixer. The mechanically-stirred mixer consisted of a series of 5 chambers each with an impeller: two chambers for rapid mixing (G value = 145 s⁻¹), three for slow mixing (G value = 40 s⁻¹). The duration of the rapid and slow mixing was 1.0 and 3.4 min, respectively. Coagulant was added to the second rapid mixing chamber. The duration of the static mixer was 4.8 s. The coagulation-pretreated waters were pumped into each membrane module at a constant rate.

The immersed ceramic MF and coagulation pretreatment system is shown in Figure 2. Tubular modules (nominal pore size, 0.1 µm) were immersed in a rectangular tank, and the water was permeated under vacuum at a constant rate. Perforated tubes were placed under the membrane modules for the aeration. These prevented floc-cake formation on the membrane surface, thus reducing the pressure rise. The coagulation pretreatment was performed in a static mixer of 2.4 s duration.

Virus solution and viral assays

Bacteriophage Qβ, which is similar in size (23 nm), shape (icosahedron), and nucleic acid (single-stranded RNA) to hepatitis A virus and polio virus, was used as a model virus, and the virus seeding studies were conducted in order to discuss virus removal by the coagulation-MF systems. River waters sampled from Kiso River (Aichi, Japan; water quality shown in Table 1) and ultra-pure water (Milli-Q Gradient A10 System, Millipore, Bedford, MA, USA) were seeded with Qβ virus to prepare virus-spiked waters for the experiments.
Qβ virus was grown in *Escherichia coli* K12F⁺(A/λ) culture to the concentration of >10¹¹ PFU/mL. For five coagulation-MF experiments (results shown in Figures 4–8), the virus-spiked waters of 10⁶ PFU/mL were prepared by a 0.5:10⁵ dilution of the virus culture solutions of >10¹¹ PFU/mL in the river waters or the ultrapure water. Although the virus culture solution contained much organic matter such as peptone and glucose, and the TOC of the virus culture solution was about 6,000 mg/L, the high degree of dilution (0.5:10⁵) theoretically rendered additional TOC increases of the virus-spiked waters below 0.03 mg/L. An experiment (results shown in Figure 3) was conducted with virus-spiked water of 10⁷ PFU/mL and the TOC increase due to the addition of virus culture solution was about 0.6 mg/L.

Qβ virus was assayed according to the double-agar-layer method, with *E. coli* K12F⁺(A/λ) as the host bacteria. The concentration of Qβ virus was presented as the mean of triplicate plates. The concentration of total viruses surviving in floc suspension (viruses in liquid phase plus viruses in floc structure) was measured after dissolving the aluminium floc (aluminium hydroxide), which included viruses in an infectious state. The floc dissolution was conducted by raising the pH to 9.5 with NaOH with beef extract (final concentration; 6%). The concentration of virus in the liquid phase of floc suspension was measured after separating floc particles by centrifugation at 3,000 x g (4,000 rpm) for 5 min.

**Results and discussion**

**Pressure-fed ceramic MF system**

Figure 3 shows the virus removal by the pressure-fed ceramic MF after the coagulation pretreatment with PACl dosing. The samples were withdrawn at 2 min, 1 h, 3 h, and 6 h of the filtration operations from the raw water tank and the membrane permeate, and the time-averaged removals were obtained. No significant removal was observed without PACl dosing, because the pore size of the membrane (100 nm) is larger than the virus size (23 nm). On the contrary, the MF with coagulation pretreatment with > 1.0 mg-Al/L dose removed the virus by about 7.5 logs. In comparison, an UF system (cellulose acetate membrane) with a molecular weight cutoff (MWCO) of 150 k was operated at 1.0 m/day flux for

### Table 1  River water quality

<table>
<thead>
<tr>
<th>Designation</th>
<th>RW1</th>
<th>RW2</th>
<th>RW3</th>
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<tr>
<td>Turbidity</td>
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<td>3.3</td>
<td>1.1</td>
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<td>Alkalinity (mg-CaCO₃/L)</td>
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<td>17.5</td>
<td>21.7</td>
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<tr>
<td>TOC (mg/L)</td>
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<td>2.2</td>
</tr>
<tr>
<td>UV abs. At 260 nm (cm⁻¹)</td>
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<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>Conductivity (mS/m)</td>
<td>6.9</td>
<td>10.3</td>
<td>8.3</td>
</tr>
</tbody>
</table>
the same virus-seeding water. After the UF, approximately $10^{-7.5}$ of virus remained in the filtrate. Therefore, the combination of the ceramic MF and the PACl dosing of more than 1.0 mg-Al/L achieved almost the same performance in virus removal as the UF of MWCO 150 k.

Upon confirming very high virus removals by the ceramic MF+coagulation pretreatment, experiments were conducted to compare the pretreatments performed by the conventional mechanically stirred mixer and the static mixer. The static mixer had a much shorter duration for the coagulation reaction than the mechanically stirred mixer had. The results at PACl dosing of 0.55 mg/L are shown in Figure 4. The MF after coagulation by the static mixer attained a virus removal of 5.5 logs at the initial filtration period, and the removal efficiency increased with filtration time. Overall, the removal by MF+static mixer coagulation pretreatment was 6–7 logs, while MF+mechanical mixer coagulation pretreatment removed virus by 7.5 logs.

The concentrations of total viruses surviving in the liquid phase and in the floc structure in the final chamber of the mechanical mixer were measured after dissolving the aluminium floc (aluminum hydroxide). With a PACl dosing of 0.55 mg/L, $10^{-2.5}$ of virus survived in

![Graph showing remaining fraction of virus Qβ](image)

Figure 3 Remaining fraction of virus Qβ (flux 1.5 m/d, RW1 with initial $10^7$ PFU/mL, pH 7.0)

![Graph showing remaining fraction of virus Qβ](image)

Figure 4 Remaining fraction of virus Qβ after coagulation and pressure-fed MF (0.55 mg-Al/L), flux 1.5 m/d, RW2 with initial $0.7 \times 10^6$ PFU/mL, pH 7.15)

Note: for the mechanical mixing coagulation+MF system at PACl dosing of about 0.5 mg-Al/L, the removal efficiency shown in Figure 3 is 1-log lower than that shown in Figure 4. This discrepancy would not be due to the slight difference in the PACl dose (0.53 vs. 0.55 mg-Al/L), but rather to the difference in the TOC of the feed solutions. The former experiment was conducted with the virus-spiked waters of $10^7$ PFU/mL, and TOC was raised to 1.5 mg/L from 0.9 mg/L by spiking a larger amount of virus culture solution. Virus removal by coagulation is negatively influenced by dissolved organic matter in the solution (unpublished data).
the coagulation mixer. Therefore, the coagulation process itself contributed to removing virus, and the observed difference in virus removal between the MF systems with mechanical and static mixers would then be attributable to the duration of the coagulation time. On the other hand, the percentage remaining of the viruses that had passed through MF after the mechanical mixer coagulation pretreatment was $10^{-7.5}$. Therefore, only a small portion ($10^{-5.0}$) of the viruses surviving after the coagulation pretreatment permeated through MF. This virus reduction was due to the virus adsorption/filtration by aluminium floc particles, as discussed in more detail below.

In order to investigate the reason why the virus was removed during the coagulation process, batch coagulation tests were conducted with the pure water and the river water spiked with the virus. The concentration of viruses in the liquid phase of the floc suspension was measured by centrifugation, and the total concentration of viruses in the floc suspension was measured after dissolving the floc. Figure 5 shows the time-variation in the virus concentration after 1.0 mg-Al/L PACl dosing. At each measurement, the virus concentration was larger after dissolving floc than after centrifugation. This finding indicates that a portion of the viruses survived in aluminium floc. In addition, the virus concentration measured after dissolving the floc particles decreased with time both in pure water and river water, which suggests that PACl dosing would have inactivated the virus (Matsui et al., 2001). Thus, the removal of virus observed in the coagulation-mixing tank was attributed to both the adsorption onto aluminium floc particles and virus inactivation in the coagulation process. Further virus reduction by the MF after the coagulation pretreatment could be attributed to the virus adsorption onto floc particles retained on the membrane surface.

**Immersed ceramic MF system**

The immersed ceramic MF removed the virus to an extent comparable to the pressure-fed ceramic MF, as shown in Figure 6. The removal was 6–7 logs, except in the initial filtration period. In spite of the high rejection of the virus, no virus accumulation in the membrane-immersed tank was observed, probably due to the virucidal activity of the coagulant. The virus concentration in the immersed tank was kept at a constant value of $10^{-3}$ of the influent concentration. The virus removal was somewhat enhanced without aeration, compared to the system with aeration. Aeration in the immersed tank was originally designed to prevent membrane fouling and then pressure rise. However, the floc buildup on the membrane surface could contribute to the enhancement of virus removal, as suggested previously. Therefore, MF without aeration may improve virus removal, although it enhances pressure.
rise. Virus concentration in the immersed tank was reduced slightly without aeration because viruses were retained on the membrane surface and suspended less in the tank.

Figure 7 shows the results at pH 7.4, a more alkaline condition than the conditions under which the data presented in Figure 6 were collected. The virus removal at pH 7.4 was 5 logs and was lower than that at pH 7.15 (Figure 6). Comparing the results at filtration flux 1.0 and 1.5 m/d, no large difference in removal was observed. However, the virus concentration in the immersed tank was slightly higher with flux 1.5 m/d than with flux 1.0 m/d, due to the higher rate of feeding to the immersed tank.

Figure 8 shows the result for pH 6.8. A higher removal, close to 7.5 logs, was obtained at pH 6.8. In this experiment, we measured the concentration of virus in the liquid phase of the immersed tank after separating the floc particles by centrifugation, as well as the total concentration of virus in the immersed tank after dissolving the floc particles. In the immersed tank, $C/C_0$ for total virus was $10^{-4}$ while it was $10^{-4.5}$ for virus in the liquid phase. This result indicates that partial virus removal was attained by the virus inactivation before filtration. The viruses remaining in the floc structure occupied more than half of the total viruses in the immersed tank, and these were easily removed by the MF membrane separation. Although $C/C_0$ of the virus in the liquid phase in the immersed tank was $10^{-4.5}$, it was reduced further to $10^{-7.5}$ after the MF separation. Therefore, this difference, namely a $10^{-3}$ reduction of virus in the liquid phase, was due to the MF filtration itself. On the other hand, no virus reduction was attained without a coagulant dose (Figure 3), proving that the virus passes through the pores of the MF membrane. This means that floc retained on the membrane surface plays an important role in the removal of the virus.
Conclusions
1. A virus removal of 6–7 logs was obtained for both pressure-fed and immersed ceramic MFs with PACl coagulation pretreatment of 0.55 mg-Al/L dose at pH 7.15.
2. The virus removal was higher at pH 6.8 (7.5 logs) than at pH 7.15.
3. The virus removal was also enhanced at higher PACl dosages.
4. Virus inactivation by the coagulant, virus adsorption onto suspended floc particles, and virus filtration by the floc retained on the membrane surface were the mechanisms of virus removal. The removal efficiencies for each mechanism were roughly 4 logs, 0.5 logs, and 3 logs, respectively, with 0.55 mg-Al/L PACl dosage at pH 6.8.
5. The virus concentration in the permeate did not increase with filtration time, and the virus concentration in the immersed tank was kept constant during the MF operation. Thus, virus was not accumulated in the retentate, possibly due to the virucidal activity of the PACl coagulant.

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