Effects of reversible and irreversible membrane fouling on virus removal by a coagulation–microfiltration system

Nobutaka Shirasaki, Taku Matsushita, Yoshihiko Matsui and Koichi Ohno

ABSTRACT

We evaluated the removal of virus (bacteriophage Qβ) after hydraulic backwashing and the effects of reversible and irreversible membrane fouling on virus removal by a coagulation–microfiltration (MF) system. The rate of virus removal in the coagulation–MF system was low at the beginning of filtration but increased with filtration time, owing to the accumulation of foulant on the membrane. The rate of virus removal thereafter remained high, even after hydraulic backwashing of the membrane to remove reversible membrane foulant. The presence of irreversible, rather than reversible, membrane foulant contributed to the increase in virus removal rate observed at the beginning of filtration. The irreversible membrane fouling maintained a high virus removal rate even after hydraulic backwashing. Moreover, irreversible fouling of the membrane during long-term filtration (1 month) improved virus removal in the coagulation–MF system, and the membrane excluded virus particles even in the absence of coagulation pretreatment. Therefore, the accumulation of irreversible membrane foulant with filtration time played an important role in virus removal by the coagulation–MF system.

Key words | coagulation, membrane fouling, microfiltration (MF), virus removal

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INTRODUCTION

Microfiltration (MF), which has been extensively applied in the field of drinking water treatment, can effectively remove turbidity, bacteria, algae, and protozoa. However, virus removal is not always possible with MF treatment alone, because MF pore sizes usually are larger than the diameters of pathogenic waterborne viruses. Therefore, pretreatments are required to achieve high virus removal rates.

Coagulation–MF systems remove viruses effectively (Matsui *et al.* 2003; Matsushita *et al.* 2005; Zhu *et al.* 2005*a*,*b*; Fiksdal & Leiknes 2006). However, the rate of virus removal is low at the beginning of filtration and increases with filtration time (Matsushita *et al.* 2005, 2006), suggesting that the accumulation of membrane foulants might contribute to the increase in virus removal rate. In MF without pretreatment, reversible membrane foulant (Jacangelo *et al.* 1995; Madaeni *et al.* 1995), which is removed during hydraulic backwashing, as well as irreversible membrane foulant (Jacangelo *et al.* 1995), which is not removed during hydraulic backwashing, are both reported to contribute to virus removal. However, the characteristics of the membrane foulant differ between systems using MF treatment alone and those combining coagulation and MF. The foulant in MF-only systems would consist mainly of natural organic matter (NOM) and suspended solids (SS) from the source water, whereas that in coagulation–MF systems also would include aluminum floc formed during coagulation pretreatment: the membrane fouling observed in coagulation–MF systems was promoted not only by the NOM and SS themselves but also by the aluminum floc, which contains many types of aluminum species associated with NOM and SS. However, the effects of reversible and irreversible membrane fouling on virus removal in coagulation–MF systems have not previously been investigated.

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Accordingly, our objectives were to investigate (1) changes in the virus removal rate after backwashing, and (2) the effects of reversible and irreversible membrane fouling on virus removal in a coagulation–MF system.

MATERIALS AND METHODS

Source water, coagulant, and MF membranes

Water was sampled from the Toyohira River (Sapporo, Japan; Table 1). Polyaluminum chloride (PACl; 10% Al_2O_3, basicity 62.5%; Sumitomo Chemical Co. Ltd., Tokyo, Japan) was used for coagulation pretreatment. The membrane used was a monolithic ceramic MF module (multichannel tubular, nominal pore size 0.1 μm, effective filtration area 0.048 m^2; NGK Insulators, Ltd., Nagoya, Japan), which was installed in a stainless-steel casing.

Virus used

Bacteriophage Qβ (NBRC 20012) obtained from the NITE Biological Resource Center (NBRC, Chiba, Japan) was used as a model virus. The genome of Qβ consists of a single-stranded RNA molecule encapsulated in an icosahedral protein shell (capsid) approximately 0.023 μm in diameter, without an envelope. Qβ is widely used as a surrogate for pathogenic waterborne viruses (Urase *et al.* 1996; Otaki *et al.* 1998) because of its morphologic similarities to hepatitis A viruses and polioviruses, the removal of which is important during the treatment of drinking water. Qβ was propagated for 22 to 24 h at 37°C in *Escherichia coli* (NBRC 13965) obtained from NBRC. The Qβ culture solution was centrifuged (2000 × *g*, 10 min) and then filtered through a membrane filter (hydrophilic cellulose acetate, pore size 0.45 μm; Dismic-25cs, Toyo Roshi Kaisha, Ltd., Tokyo, Japan). The filtrate was purified with a centrifugal filter device (molecular weight cutoff 100,000; Centriplus-100, Millipore Corp., Billerica, MA, USA) to prepare the virus stock solution. Because of this purification, the DOC increase as a result of spiking the river water with the stock solution was reduced to less than 0.1 mg L^{-1}.

Table 1 | River water quality

	River water 1	River water 2
Sampling time	09-Mar-06	12-Dec-06
pH	7.7	7.7
DOC (mg L^{-1})	0.60	1.10
OD260 (cm^{-1})	0.013	0.027
Turbidity (NTU)	0.15	1.13
Alkalinity (mg $CaCO_3$ L^{-1})	19.8	17.6

Virus assay

To measure the concentration of infectious viruses, the PFU method was used in accordance with the agar overlay method (Adams 1959) with the bacterial host *Escherichia coli*. Average plaque counts of triplicate plates prepared from the same sample yielded the virus concentration.

Experimental setup

The experimental setup is shown in Figure 1. The river water in the raw water tank was spiked with virus to a final concentration of $10^{5.8}$ to $10^{7.1}$ PFU $ml^{-1}$and was fed into the system at a constant flow rate (62.5 $L(m^2 \cdot h)^{-1}$) by a peristaltic pump. Hydrochloric acid was added before the first in-line static mixer (hydraulic retention time 2.4 s, Noritake Co., Ltd., Nagoya, Japan) to maintain the pH of the MF permeate at 6.8. PACl was injected after the first in-line static mixer and before the second in-line static mixer at a constant dose rate (0, 0.54, 1.08, or 1.62 mg-Al L^{-1}). After the PACl had been mixed in, the water was fed into the ceramic MF module in dead-end mode. Filtration was performed for 0.25, 3, 6, and 12 h with hydraulic back-washing (pressure 500 kPa) with MF permeate or ultrapure

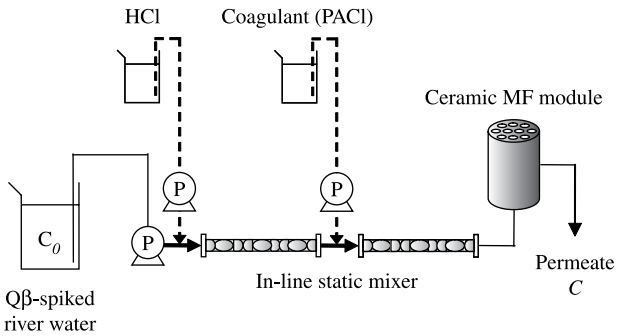

Figure 1 | The experimental coagulation–MF system. C_0 and C are the virus concentrations (PFU ml^{-1}) in the raw water tank and the MF permeate, respectively.

water. Virus concentrations in the raw water tank and MF permeate were measured hourly.

Filtration experiments with the fouled membrane during short-term filtration

Two ceramic MF membranes were fouled with aluminum floc by continuously feeding river water (without spiked virus) into the coagulation–MF system. The PACl dose was 1.62 mg-AlL^{-1} during 6 h of filtration. After 6 h of filtration, one fouled membrane was backwashed with MF permeate (used and backwashed membrane), but the other was not (used membrane without backwashing). Then, during the next 6 h, river water spiked with virus was fed into the system, but no coagulant was injected: virus particles were filtered directly by the membrane. Virus concentrations in the raw water tank and MF permeate were measured hourly.

Filtration experiments with the irreversibly fouled membrane during long-term filtration

The coagulation–MF filtration experiment with hydraulic backwashing was conducted for 1 month at a constant flow rate (62.5 L$(m^2 \cdot h)^{-1}$) by using the groundwater at Hokkaido University (DOC 0.48 mg L^{-1}, OD260 0.007 cm^{-1}) without spiked virus. The PACl dose was 1.08 mg-AlL^{-1}, and the backwashing interval was 5 h. After the 1-month filtration, the fouled membrane was backwashed with ultrapure water to remove the reversible membrane foulant (irreversibly fouled membrane). Then, during the next 6 h, river water spiked with virus was fed into the system with or without coagulant. Virus concentrations in the raw water tank and MF permeate were measured hourly.

RESULTS AND DISCUSSION

Effect of hydraulic backwashing on virus removal in the coagulation–MF system

The log of the virus removal rate [log(C_0/C)] in the coagulation–MF system was 4 at the beginning of filtration and gradually increased to 5 over the next 3 h (Figure 2), perhaps because of the presence of reversible or irreversible

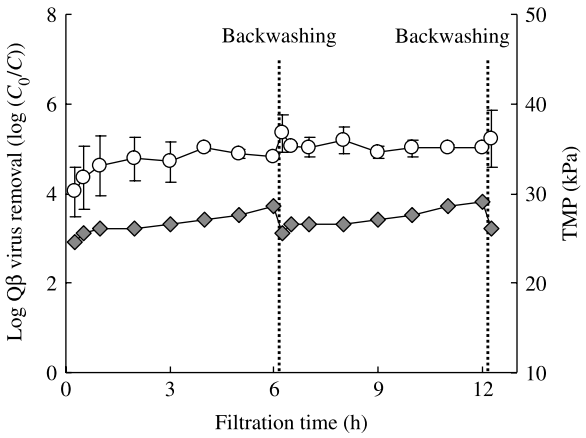

Figure 2 | Changes in the rate of removal of Qβ virus and TMP with filtration time in the coagulation–MF system. Values are the means of 2 experiments. Open circles, rate of Qβ virus removal; solid diamonds, TMP; source water, river water 1; PACl does, 0.54 mg-AlL^{-1}. Backwashing was conducted with MF permeate.

membrane foulant, or both. Our research group previously reported a similar increase with filtration time in the coagulation–MF system (Matsushita *et al.* 2005, 2006). Just after hydraulic backwashing after 6 h of filtration, the transmembrane pressure (TMP) recovered to its initial value (Figure 2). However, the virus removal rate did not decrease to its initial value after backwashing, even though the reversible membrane foulant had been removed, but remained high throughout the subsequent 6 h of filtration. These results suggest that the presence of irreversible membrane foulant would be contributed to virus removal after 6 h of filtration in this coagulation–MF system. The amount of membrane foulant accumulated irreversibly during the 6 h filtration might have been too small to be recognized as an increase in manometric measurement.

To investigate the effects of reversible and irreversible membrane fouling on virus removal during the first 3 h of filtration, when the virus removal rate increased rapidly with filtration time, the membrane was subjected to hydraulic backwashing after 0.25 and 3 h of filtration to remove reversible membrane foulant from the membrane (Figure 3). Although the TMP recovered to its initial value after backwashing at the 3 h time point (Figure 3b), the rate of virus removal did not change significantly (Figure 3a), indicating that irreversible membrane foulant contributed to virus removal. After 0.25 h of filtration, the rate of virus removal increased after backwashing (Figure 3a). Samples

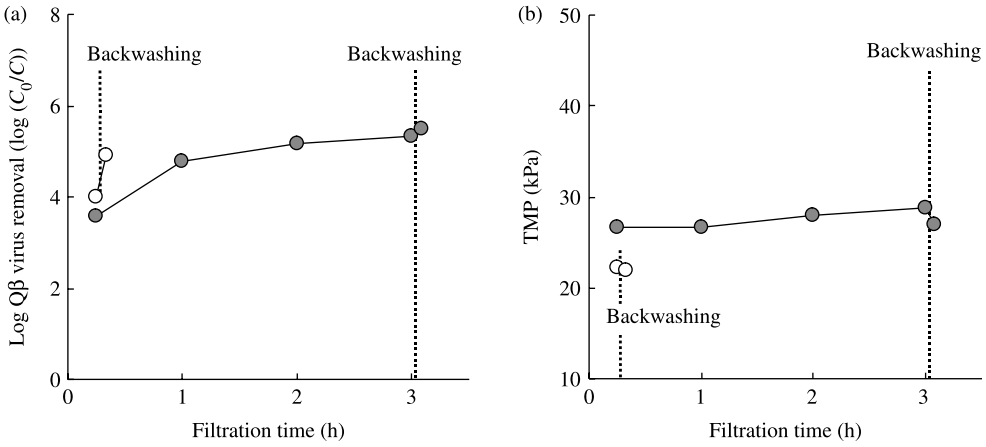

Figure 3 | Effects of reversible and irreversible membrane fouling on Qβ virus removal 0.25 after and 3 h of filtration in the coagulation–MF system. Open circles, 0.25 h of filtration; solid circles, 3 h of filtration; source water, river water 2; PACl does, 1.08 mg-AlL^{-1}. Backwashing was conducted with ultrapure water.

just after backwashing were collected from the system when the filtration was conducted subsequently for 5 min after backwashing. Some foulants might be further accumulated on the membrane during this additional 5 min of filtration; details are not clear. Nonetheless, decrease in virus removal rate was not observed after backwashing at any filtration time (0.25, 3, and 6 h), suggesting that irreversible membrane fouling would contribute to virus removal and that the irreversible accumulation of foulant with filtration time would increase virus removal. In other words, reversible membrane fouling may not affect the virus removal rate in the coagulation–MF system. Our research group reported that the effect of coagulant dose on virus removal in the same coagulation–MF system (Matsushita *et al.* 2005), and suggested that the coagulant dose strongly affected virus removal. However, in this research, the difference in the coagulant dose did not affect the virus removal: although the coagulant doses in Figures 2 and 3 were 0.54 and 1.08 mg-AlL^{-1}, respectively, trends in virus removal were almost the same. These results were possibly due to the difference in source water quality such as DOC, OD260 and turbidity between these two experiments (Table 1). Jacangelo *et al.* (1995) reported that reversible membrane fouling ("cake layer") became the dominant mechanism at early time points during MF filtration without coagulation pretreatment. Our results apparently contradict theirs, probably because of differences in the membrane foulant characteristics in the presence versus absence of coagulation pretreatment.

Characteristics of membrane foulant accumulated during short-term coagulation–MF filtration

To investigate the characteristics of the membrane foulant which accumulated during short-term coagulation–MF filtration, we conducted several filtration experiments. A virgin membrane, devoid of any membrane foulant, could not remove virus particles (Figure 4a). Just after hydraulic backwashing after 6 h of filtration, the TMP of the used and backwashed membrane recovered to its initial value (Figure 4b), and the removal rate of virus particles by the used and backwashed membrane was almost the same as that by the virgin membrane (Figure 4a). Therefore, irreversibly fouled membrane during short-term filtration could exclude the floc with its entrapped virus particles (Figures 2 and 3a) but passed free virus particles (Figure 4a). Although the occurrence of irreversible fouling might reduce the effective pore size of the membrane, the size still might be larger than the diameter of the virus particles.

The used membrane without backwashing, on which membrane foulant accumulated reversibly and irreversibly, achieved a rate of virus removal of 4 log, and it maintained this high rate for 6 h. Therefore, virus particles were rejected by the used membrane without backwashing but not by the used and backwashed membrane (Figure 4a). The difference between the two membranes was the occurrence of reversible membrane fouling; therefore reversible membrane fouling contributed to the removal of virus particles. In contrast, reversible membrane fouling did not contribute to the removal

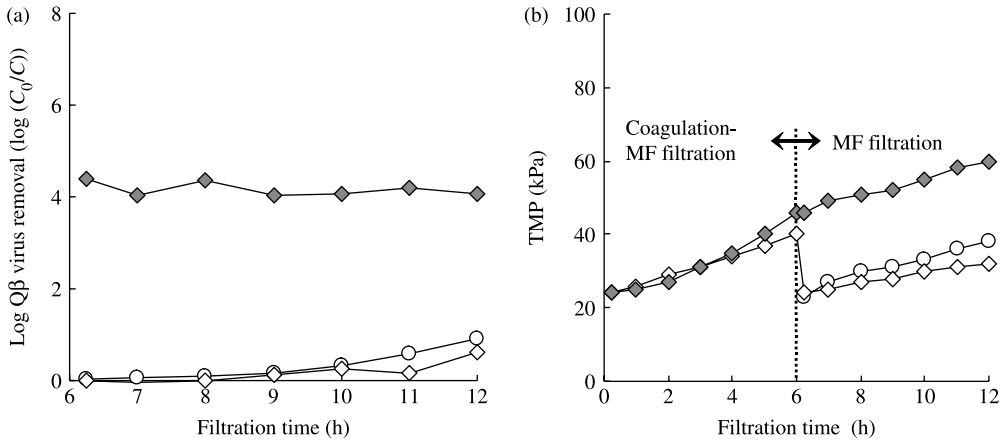

Figure 4 | Characteristics of membrane foulant accumulated during short-term coagulation–MF filtration. Open circles, virgin membrane; open diamonds, used and backwashed membrane; solid diamonds, used membrane without backwashing; source water 1; PACl does, 1.62 mg-AlL^{-1}. The virus was spiked at 6 h of filtration, and MF-only system was operated after that.

of virus particles trapped in floc (Figures 2 and 3a). Perhaps most of the flocs entrapping virus particles were larger than the effective pore size of the used and backwashed membrane: the number of floc particles whose sizes were between the effective pore sizes of the above two membranes was extremely small.

Effects of irreversible membrane fouling during short-term versus long-term filtration

In the above-mentioned experiments, we investigated the effects of membrane foulant which accumulated during short-term filtration (maximum, 6 h). In actual water-treatment plants, membranes are used for prolonged period and undergo repeated backwashing. The membrane gradually is fouled during filtration, such that membrane foulant accumulates irreversibly in the membrane pore structures over time. Figure 5 shows the effect of the irreversible accumulation of membrane foulant on virus removal during long-term coagulation–MF filtration (1 month). The TMP of the irreversibly fouled membrane was much higher than that of virgin membrane at the beginning of filtration (Figure 5b), indicating that membrane foulant accumulated

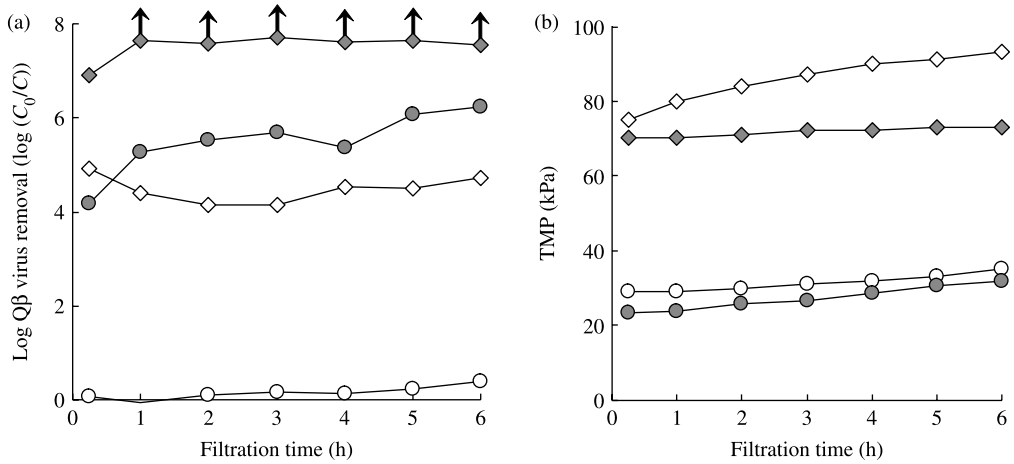

Figure 5 | Characteristics of irreversible membrane foulant accumulated during long-term coagulation–MF filtration. Arrows indicate values greater than those that could be estimated accurately in light of the detection limit of the PFU method. Open circles, virgin membrane in MF-only system; solid circles, virgin membrane in coagulatio–MF system (PACl dose, 1.08 mg-AlL^{-1}); open diamonds, irreversibly fouled membrane in MF-only system; solid diamonds, irreversibly fouled membrane in coagulation–MF system (PACl dose, 1.08 mg-AlL^{-1}); river water 2.

irreversibly and considerably on the membrane in the long-term coagulation–MF filtration experiment.

Whereas the rate of virus removal by a virgin membrane was 5 log in the coagulation–MF system, the rate of virus removal by a membrane that was irreversibly fouled due to long-term filtration was more than 7 log (Figure 5a). These results indicate that the membrane foulant which accumulated irreversibly during long-term filtration improved the virus removal rate in the coagulation–MF system. Although membrane that was irreversibly fouled during short-term filtration could not exclude virus particles (Figure 4a), membrane that was irreversibly fouled during long-term filtration could do so, suggesting that the amount of membrane foulant which accumulated irreversibly during short-term filtration was so small that its effect on the removal of virus particles could not be appreciated. In contrast, when filtration lasted for at least 1 month, the effect was much greater and could be discerned. Jacangelo *et al.* (1995) reported that irreversible fouling of a membrane increased the removal of bacteriophage MS2 during long-term MF filtration; our results agreed with theirs. Even though accidents may occur during coagulation pretreatment in actual coagulation–MF systems and lead to insufficient pretreatment, virus removal still can be expected to some extent, owing to the irreversible accumulation of membrane foulant on the membrane.

CONCLUSIONS

1. The virus removal rate in the coagulation–MF system was low at the beginning of filtration but increased with filtration time owing to the accumulation of foulant on the membrane. The virus removal rate did not decrease and remained high even after hydraulic backwashing of the membrane.
2. Irreversible, rather than reversible accumulation of membrane foulant contributed to the increase in virus removal rate observed at the beginning of filtration. The irreversible membrane fouling maintained the high removal rate of virus, even after hydraulic backwashing.
3. Irreversible fouling of the membrane during long-term filtration improved the virus removal rate in the coagulation–MF system. Moreover, irreversibly fouled membrane excluded virus particles even in the absence of coagulation pretreatment.

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