MS2 Removal from High NOM Content Surface Water by Coagulation - Ceramic Microfiltration, for Potable Water Production

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MS2 bacteriophages removal from surface water, characterized by high natural organic matter (NOM) content, was investigated by inline coagulation/flocculation pretreatment followed by ceramic microfiltration (MF). MS2 and DOC removal increased with lower pH and higher coagulant dose. Lowering the coagulant pH from 6.5 to 5.5 for polyaluminum chloride (PACl), and to 5.0 for iron chloride (FeCl), respectively, along with doubling of the coagulant dose from 2 to 4 mg Al/L, and from 4 to 8 mg Fe/L, respectively, maximized the virus removal, resulting in more than six log unit reductions up to complete virus retention. However, high residual metal concentrations were found under such conditions. Comparison of conventional two-stage coagulation pretreatment with simple inline coagulation did not show any significant performance differences. Both investigated coagulants showed virus inactivation about two log units after 60 min contact time, which is equivalent to a virus inactivation of 99%. This inactivation was only reversible to a small extend by chemical or physical floc destruction. The investigated process combination can comply with modern hygienic barrier standards. © 2011 American Institute of Chemical Engineers *AIChE J,* 58: 2270–2281, 2012
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Introduction

Water hygiene is of great concern in the production of potable water, where enteric pathogens in drinking water can cause diseases, acute infections and are able to survive for long term in the environment.[1,2] Several cases where bacteria and viruses have caused serious outbreaks in the past have been documented.[3,4] Although enteric pathogens rarely debilitate healthy adults seriously, they can be critical for the health of young children and elderly who often have compromised immune systems.[5] Due to their low infection dose and low removal efficacy in conventional treatment processes, enteric viruses represent a particular health risk and their removal is a great challenge in the area of drinking water treatment technologies.

Furthermore, the removal of natural organic matter (NOM) is an increasing problem in the field of water purification. Especially in Nordic countries such as Norway, where the sources of potable water—mostly surface water—contain high amounts of NOM due to the natural conditions. The literature shows, that during the last two decades the NOM concentration of lakes especially in south-eastern Norway and southern Sweden increased dramatically and unprecedentedly.[6] These natural water compounds are not harmful by themselves but can be of aesthetic concerns regarding taste and odor. Furthermore, natural organic substances appear to be precursors for disinfection byproduct (DBP) formation, such as THMs (trihalomethanes), which are known as to be carcinogenic. Therefore, specific limiting values are defined in the national drinking water guidelines and the NOM removal is a major target of water research in those countries.[7]

Efficient techniques for NOM removal can be coagulation/flocculation combined with sedimentation or filtration, ion exchange, ozonation/biofiltration and nanofiltration.[8] For pathogen removal or inactivation the combination of coagulation/flocculation and sedimentation/filtration methods, as well as the application of reverse osmosis, nanofiltration and partially ultrafiltration are assumed to be satisfactory, especially if these techniques are complemented with disinfection methods such as UV-radiation or chlorination. Although these treatment methods have proved to be fairly effective against NOM and viruses, they still show operational or economical disadvantages.[9] Granular media filtration for example, which is widely used in drinking water treatment, removes viruses and protozoan pathogens only efficiently if operated under optimal coagulation conditions. Nanofiltration and reverse osmosis are usually only operable at relatively

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high pressures at relatively low fluxes with a high chemical demand. The combination of coagulation/flocculation prior to MF may be favored as an alternative treatment process for production of high-quality potable water targeting both NOM and pathogens, since it merges all the benefits of direct coagulation and the membrane filtration technology.[10–14] However, virus and NOM removal by MF only is rather poor. Furthermore, all membrane processes are prone to fouling, which refers to the blockage of membrane pores during filtration caused by the combination of sieving and adsorption of particulates and compounds onto the membrane surface or within the membrane pores. Coagulation pretreatment is therefore necessary, since it is both reducing the membrane fouling by NOM adsorption and increases virus and NOM removal drastically. However, the coagulation has to be optimized since it otherwise increases the membrane fouling and causes other problems such as high residual metal concentrations. If optimization is done, ceramic MF can be operated with significantly higher fluxes and higher investment costs compared to their polymeric counterparts can be balanced off.[15]

Only few studies have investigated the simultaneous elimination of NOM and viruses by coagulation/flocculation and MF treatment. This is fundamental for the realization of modern multiple barrier concepts, which are connecting different consecutive treatment steps in a way that even with a breakdown of one stage, a sufficient pathogen removal is still ensured.[16] However, such treatment steps are directly influencing each other. Insufficient NOM removal increases for example the chlorine demand and leads to more DBP formation. Inadequate virus removal by the MF has to be balanced by a more efficient final disinfection step. Higher coagulant dosages may be necessary to ensure enhanced coagulation and sufficient DBP precursor removal if the NOM content is high in the raw water. Efficient virus removal has been documented by coagulation and subsequent ceramic MF,[11,12,17] but no or only little NOM was present. However, such investigations are important since NOM hampers the virus removal by coagulation[18] and, consequently, compromises the hygienic barrier potential of the treatment scheme. This may be especially important for the treatment of Nordic waters compared to other surface waters, since due to their low-turbidity viruses will be associated with particles to lesser degree and, thus, more difficult to remove. Furthermore, no direct comparison of aluminum and iron based coagulants have been published for full-scale systems and similar membranes. Only few bench-scale experiments with organic membranes using iron-based coagulants are reported.[14] Besides virus removal, virus inactivation by aluminum and iron-based coagulants is another important issue, since it is a vital difference if viruses are just inactivated by the coagulant, physically removed by the membrane or both. Furthermore, a possible inactivation by metal coagulants may lead to overestimation of virus removal and, thus, to faulty conclusions. Results of relevant studies investigating this issue do not correspond to each other. While one study showed a bit more than two log units of virus inactivation after 60 min by a PACl dosage of 1 mg AL/L in ultrapure water,[19] others found no statistical relevant virus inactivation after 3.5 h contact time after applying iron chloride and alum.[14] Consequently, this study was undertaken to address these issues. Combined virus and NOM removal was investigated at a full-scale pilot plant, in dependence on four main process parameters: coagulant type (Al and Fe based) and dose, coagulation pH and pretreatment setup. Besides, virus inactivation was examined in jar tests, also looking at a potential reversal of a potential inactivation.

As evaluation criterion for sufficient virus removal, the requirements of the surface water treatment rule (SWTR) formulated by the U.S. EPA in 2001 were used.[20] Therefore, virus removal or inactivation of 99.99% is demanded. Results were also evaluated with regards to recommendations published by the Norwegian national association of water and wastewater works.[21] There, the log credit suggested for coagulation/membrane filtration (MF/UF) is 3-log units for bacteria, viruses and parasites.

Methods

Raw Water. The raw water used in this study was prepared using a NOM concentrate from a full-scale ion exchange treatment plant, which was mixed with tap water to make up an analogue water with a turbidity of around 1 NTU, a color of 30 ± 1 mg Pt/L at pH 7 (corresponding to an absorbance of 1.1 ± 0.08 m^{-1} at a wavelength of 436 nm), a UV_{254}-absorbance of 18.1 ± 0.2 m^{-1} and a DOC concentration of 4.2 ± 0.1 mg/L. Analogue feed water ensures that the same experimental conditions apply for all experiments conducted. Previous studies have shown that this method can be successfully used and simulates real conditions quite well.[22] The NOM concentrate has been characterized as humic acid like and highly hydrophobic,[13] further having a specific UV absorption (SUVA) of 4.3 m^{-1}·L/mg C.

Pilot Plant Setup. Experiments were done with a membrane filtration pilot plant using an inline coagulation/flocculation pretreatment configuration, shown in Figure 1a. Prior to the membrane filtration unit, acid and coagulant were dosed followed by rapid mixing in the membrane feed pump, followed by a pipe flocculator with a hydraulic retention time (HRT) of 40 s, and a G value of around 500 s^{-1}. After that, the coagulated water was filtered by the membrane unit. A second option using a two-tank coagulation/flocculation setup with rapid mixing at a G value of 400 s^{-1} for 6 min followed by a slow mixing step with a G value of 100 s^{-1}, and a retention time of 14 min was also investigated as an alternative to the inline configuration. The tank setup is shown in Figure 1b.

In this study multichannel ceramic membranes, operated in dead-end, inside-out mode with a nominal pore size of 0.1 μm were investigated. The membrane flux was constant at 143 $L \cdot m^{-2} \cdot h^{-1}$. Each membrane module had 55 channels, was 1 m long and had an effective surface area of 0.43 m^2. The feed water was pumped in up-flow. Since only short time experiments (60 min) were performed no backwash was carried out during a test. After each experiment the membrane modules were intensively cleaned by soaking them, alternating in citric acid solution ($w = 1\%$), and sodium hypochlorite solution ($c = 3{,}000$ ppm). The pilot plant was equipped with two identical and independent process trains, allowing direct comparison of results. Each experiment was repeated twice with alternating the process train for statistical reasons.

Experimental Conditions. First, two different coagulants at two dosages and pH values were compared, polyaluminum chloride (PACl, PAX-18) and iron chloride (FeCl, PIX-111) from Kemira Chemicals AS, Norway. Both coagulants were dosed roughly at the same molar concentrations. For PAX-

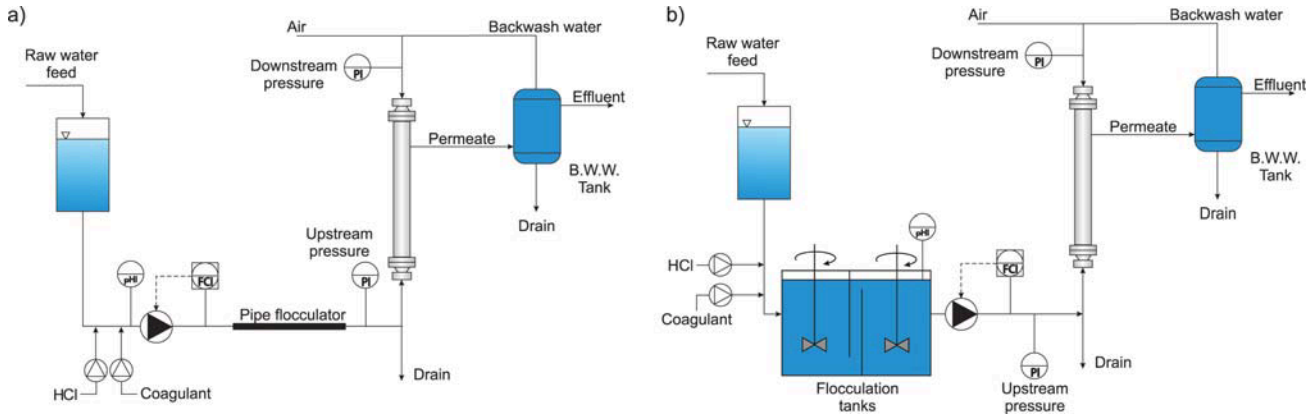

Figure 1. Flow diagram of the different membrane filtration plant configurations (a) inline coagulation setup, and (b) tank coagulation setup.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

18 the selected dosages were 2 and 4 mg Al/L (0.074 and 0.148 mM Al/L) at pH values of 5.5 and 6.5, for PIX-111 the investigated dosages were 4 and 8 mg Fe/L (0.071 and 0.143 mM Fe/L) at pH values of 5.0 and 6.5. The chosen pH values are a little lower than average commonly applied since NOM removal should be facilitated. The lower pH was chosen for FeCl compared to PACl, since optimal NOM removal takes place at different pH values for both coagulants.[13] Based on the results from this study, the best conditions for NOM and virus removal were selected for both coagulants and applied in an additional experiment, comparing the alternative process configurations, i.e., inline coagulation and tank coagulation. Figure 2 shows a summary of the experimental conditions. pH-adjustment was carried out with hydrochloric acid.

Microorganisms. In this study MS2 bacteriophages (ATCC 15597-B1, LGC Standards, Sweden) were chosen for the experiments, since it is commonly used as model virus due to its similarity in size, shape, structure and nucleic acid makeup as other water-related pathogenic viruses such as poliovirus and hepatitis A virus. Furthermore, it is harmless for the human body and the assay method is fairly easy.[2]

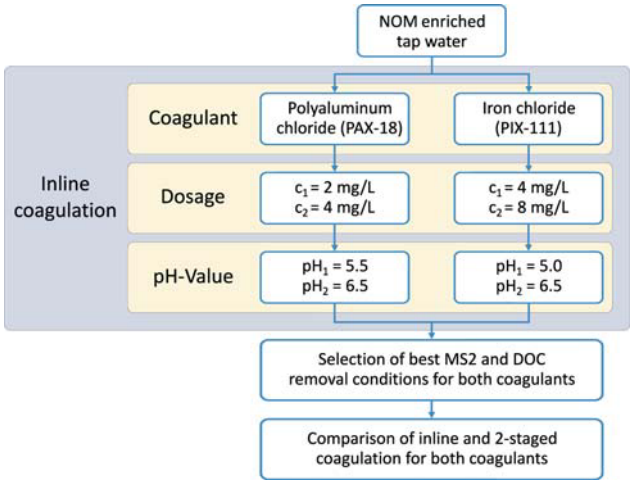

Figure 2. Flow chart of the conducted experimental series

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MS2 viruses have an icosahedral structure with a diameter of around 27 nm, and an isoelectric point in the range of 3.5–3.9.[23] They infect gram negative male *E. coli* cells by attaching on the pili and injecting their ssRNA.[24]

For the preparation of the MS2 stock solution 25 mL of Tryptone-yeast extract-glucose broth (TYGB) were inoculated with 0.25 mL of cultured *Escherichia coli* C3000 (ATCC 15597, LGC Standards, Sweden) and incubated for 20 h at 37°C ± 2°C while shaking. From that culture, 0.25 mL were taken and transferred into 25 mL of fresh TYGB, followed by incubation for 90 min while shaking. After that, 0.1 mL of a MS2 working solution was added and the culture incubated for another 5 h while shaking. Next, 2.5 mL chloroform was added. After well mixing, the culture was cooled down to 5°C, and the water phase was separated by decantation and centrifuged for 21 min at 4,800 rpm at a temperature of 5°C, to purify the viruses in the culture solution from *E. coli* debris. After that, the supernatant was decanted into a sterile bottle and stored at 5°C until use. The stock solution had an MS2 average concentration of $1 \cdot 10^{11}$ pfu/mL.

Before the experiment the stock solution was spiked into the reservoir tank containing the NOM enriched raw water, resulting in a virus concentration in the range of $2 \cdot 10^7$ to $1 \cdot 10^8$ pfu/mL in the feedwater. The pilot plant was started immediately after feedwater preparation and permeate samples were taken after 20, 35 and 50 min. The samples were stored at 4 ± 2°C until assaying within 4 h. The virus concentration was determined by counting plague forming units (pfu) after a modified overlay agar method detailed described in NS-EN ISO 10705-1 from 2001, using *Escherichia coli* C3000 as host bacterium. This method has a detection limit of 1 pfu/mL. Only infective and viable viral particles are detectable. Inactivated viruses cannot be quantified directly. Another disadvantage of the method is that coagulated virus particles are counted as one and, hence, overestimation of virus removal might be a consequence.[19] To avoid this problem, the samples were vortexed and rapidly diluted for further analysis. After each experiment the pilot plant was disinfected by adding sodium hypochlorite to the water, giving a concentration of free chorine of 50 mg/L, and operating it for 60 min. After that, the plant was operated with tap water for 6 h to rinse out the disinfection solution. The virus removal results are stated as log reduction value (LRV) which

is calculated according to Eq. 1, where c is the virus concentration in pfu/Ml

$$LRV = \log \frac{c_{raw\ water}}{c_{permeate}} \quad (1)$$

The concentration of MS2 bacteriophages in the NOM enriched raw water was found to be stable. At the beginning of the experimental series the virus concentrations were measured directly after spiking into the raw water and again after 50 min. No significant difference was found. MS2 bacteriophages are reported to be generally very stable. Yates et al.[34] found a decay rate of MS2 viruses of 0.068 ± 0.04 log pfu/day in nine different ground waters.

Inactivation Tests. The aim of this study was also to quantify the virus inactivation after application of metal based coagulants as contradicting results are found in the literature. Inactivation is defined in this study as the inability of a virus to infect a host. It was not differentiated between reasons for this inability. The viruses may still be completely intact and just adsorbed to or entrapped in flocs created after coagulant addition, rather than really decomposed, but they are not infective for the host anymore. Furthermore, a possible virus reactivation was investigated. In opposition to inactivation, reactivation implies in this context the possibility that inactivated and, thus, just adsorbed viruses are reactivated or desorbed again after physical or chemical measures.

The inactivation tests were performed in a jar flocculator manufactured by Kemira Chemicals AS, Norway, and coagulant dose and pH were the same as found for optimal virus and NOM removal in this study. The virus concentration in the raw water was equal to or higher than $3 \cdot 10^7$ pfu/mL. First acid and coagulant were dosed, followed by rapid mixing at 200 rpm for 1 min followed by mixing at 20 rpm for 60 min. Samples were taken after 5, 15, 30 and 60 min. As a reference, parallel jar tests were conducted without the addition of coagulant. Samples were taken after 0 and 60 min and the virus log reduction measured.

Additional jar tests were performed to investigate a possible reactivation effect after viruses were inactivated by coagulation. After performing the jar tests as described earlier the samples were either treated with additional shear force or the pH was increased to 10. These measures should cause floc breakage or dissolving, resulting in a possible virus desorption and, thus, reactivation. In the case of additional shear force, the samples were vortexed after taking a sample for 5 min and analyzed quickly after to avoid the reaggreagtion of particles. For the pH adjustment to 10, sodium hydroxide solution was added to the samples after taking. Besides variation of the vortexing time and the pH, the virus concentration was determined as described previously for the pilot plant trials. Samples were taken after 0 and 60. All experiments were also carried out without coagulant addition. This ensured that neither extended vortexing nor the pH increase up to 10 by themselves did influence the virus viability. No significant influence of these conditions was found.

Experimental Analysis. Turbidity measurements (90° scattered light method, turbidimeter 2100N, Hach), and the residual metal concentration (measured by high resolution ICP-MS at the Institute for Chemistry at NTNU) in the permeate were analyzed for each sample. The removal of NOM was monitored by measuring color, UV-absorption at 254 and 436 nm (spectrophotometer U-3000, Hitachi), and DOC (laboratory analyzer: Dohrmann Apollo 9000, Teledyne-Tekmar; online spectrometric probe: Spectro::lyser™, s::can Meßtechnik GmbH, Vienna, Austria).

Results and discussion

MS2 Removal without Membrane or Coagulation. It is know that viruses may interact with charged surfaces. Therefore, experiments were carried out to investigate any losses of viruses due to adsorption taking place in the pilot plant system or inside the membrane module itself. Spiked raw water was treated without and with a membrane module inserted in the pilot plant. Only the pH value was adjusted. Without the membrane module no viruses are removed or inactivated over time at all. This indicates that the adsorption of MS2 bacteriophages onto material surfaces in the pilot plant setup (e.g., synthetic tubes and metallic valves or connections) during an experiment is negligible. Furthermore, no virus damage due to installed fixtures such as pumps, tube constrictions or valves was observed. However, with the MF membrane inserted an increasing removal over time up to 1 log unit was observed. This removal might be due to direct adsorption onto the membrane surface or to particles contained in the raw water. Virus adsorption to ceramic material is strongly influenced by the type material used.[25] In general, electropositive ceramic materials show improved virus adsorption capacity since the MS2 viruses are negatively charged at pH values above the isoelectric point (IEP), and, thus, the virus adsorption can be very high. Furthermore, interactions between NOM and the viruses prior to the coagulation step should be considered, since viruses in water can adsorb charged species of either sign such as NOM. This specific adsorption may alter the surface charge of a virus.[23] Thus, the IEP of MS2 is likely to be changed due to the presence of NOM. Another study reported that viruses and NOM contain hydrophobic groups on their surfaces and, thus, can attach to each other by hydrophobic interactions.[18] Formed NOM-virus complexes may be large enough to be retained by the membrane, independent from the actual adsorption mechanism.

The removal increase over time could be explained by the formation of a thin cake layer on the membrane surface, promoting more virus retention due to adsorption or straining. NOM could form aggregates with multivalent ions found in the tap water which can be retained by the membrane. Pore constriction due to adsorbing NOM or viruses might also play a role. Such conclusions are supported by an immediate beginning of TMP increase after the start of filtration together with increased NOM removal over time, which have been observed in other pilot experiments without coagulant and virus addition. Theoretically, physical removal by itself should not be a dominant removal mechanism since the nominal membrane pore size of 100 nm is significantly larger than the virus size of 27 nm. These results correspond well to findings reported with other MF membranes. While some studies showed MS2 removals of 0.2 to 2 log magnitudes without coagulation,[14,26,27] others stated no MS2 removal at all.[10] Subsequently, only filtration with the ceramic MF membranes without coagulation does not fulfill any requirements for being considered a hygienic barrier.

Effect of Coagulant Dosage and pH Value on MS2 Removal. Within this experimental series the effect of coagulant type, dosage and pH value on virus removal with an inline coagulation setup was compared. Figure 3 summarizes virus removal for PACl, and Figure 4 for FeCl,

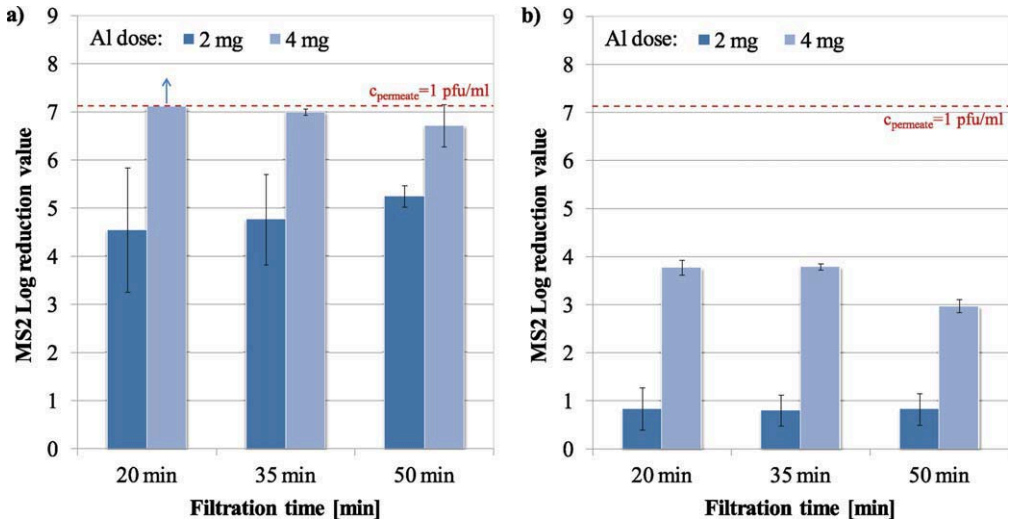

Figure 3. MS2 removal by inline coagulation with PACl as a function of coagulant dose and pH (a) pH 5.5, and (b) pH 6.5.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

respectively. For both coagulants the MS2 removal increased with a lower pH value and a higher dose. For PACl these changes are especially apparent. At a pH of 6.5 only 0.8 log units are removed at an Al dose of 2 mg/L, compared to 3.0 to 3.8 log units at the same pH but for a higher dose of 4 mg Al/L. Decreasing pH to 5.5 improved the MS2 removal even more. Around 4.5 to 5.2 log units were removed with a dosage of 2 mg Al/L, while almost all viruses are removed at 4 mg/L Al, where the virus concentration in the sample taken after 20 min was found to be below 1 pfu/mL (indicated with an arrow on top of the data bar as seen in Figure 3a). Even though the removal performance differs by two log units at a pH of 5.5 the absolute percentage removal varies only in the third decimal place. At least 99.99% of viruses are removed. At the lower investigated pH values, coagulation hydrolysis reactions form more positively charged polynuclear species. These can efficiently react with the negatively charged virus particles and thus alleviate virus removal. Furthermore, the coagulation pH is closer to the isoelectric point of the virus particles, resulting in a reduction of the total negative charge followed by a probable reduction of electrostatic repulsion forces. However, the pH values investigated in this study are not low enough to be close to the isoelectric point of the virus particles.[28] As a result, the MS2 viruses have a negative electrophoretic mobility under all investigated conditions and can, thus, readily react with positively charged coagulant.

High MS2 removal from waters having a low DOC was reported at relatively low coagulant dosages, applying inline coagulation and similar membranes as used in this study.[11,17] A > 6-log removal of viruses from spiked river water (DOC $\approx$1 mg/L) was achieved by two types of 0.1-μm pore-size ceramic MF systems with 0.5 to 1.0 mg Al/L of polyaluminum chloride. These findings were confirmed by others, showing up to 6-log reduction of MS2 bacteriophages by using inline coagulation at pH 6.8 with a PACl dosage of

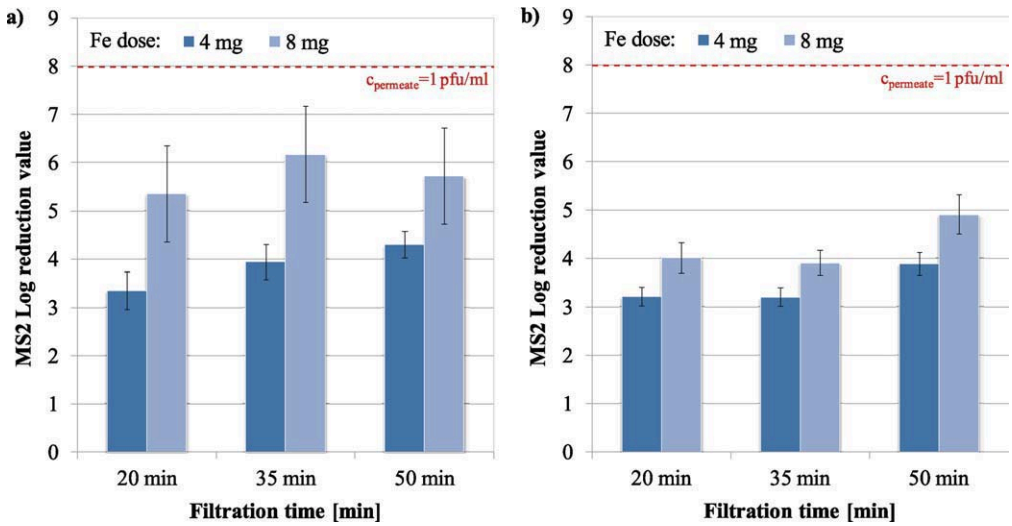

Figure 4. MS2 removal by inline coagulation with FeCl as a function of coagulant dose and pH (a) pH 5.0, and (b) pH 6.5.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1.08 mg Al/L.[29] In this study, however, sufficient virus removal was only achievable by comparably higher coagulant dosages. This is probably due to the higher organic content in the raw water and, thus, higher competition between negatively charged virus and NOM particles for free binding sites on the positively charged coagulation hydrolysis products.[18] Virus attachment is thereby reduced and higher coagulant dosages are, therefore, necessary to achieve satisfactory virus and NOM removal. The virus removal may be further influenced by specific adsorption of NOM to the viruses as described earlier. The MS2 removal rates found in this study are depending on the conditions 2 to 3 times higher than results presented in the literature, where coagulation, flocculation and rapid media filtration were used with 2.5 mg AL/L dosed as alum at unknown coagulation pH,[30] or a study by Bell et al.[31] comparing results from 9 WTP's using optimized coagulation with PACl, followed by flocculation and sedimentation.

FeCl showed a similar trend as PACl. However, the differences in MS2 removal for the conditions tested were smaller (Figure 4). Lowest removals with 3.2 to 3.8 log units were found at a pH of 6.5 and an iron dose of 4 mg/L. Removal maximum was observed at a pH of 5.0 and a dose of 8 mg Fe/L, with a MS2 removal of 5.3–6.2 log units. Other researchers reported a >4-log removal of viruses at pH 6.3 with 10 mg Fe/L of ferric chloride and 0.22 μm nominal pore size using a PVDF MF membrane.[14] That is lower than the 5-log removal at pH 6.5 and a dosage of 8 mg Fe/L achieved in this study. The Virus removal might be handicapped by 120 mg/L silica dosed into the raw water by Zhu et al.[14] which is negatively charged like the virus particles and, therefore, competes for positively charged coagulant binding sites as described earlier in this section.

Even though the removal with iron chloride is more robust to condition changes, PACl appears to have a superior removal capacity at optimized conditions. However, if the two coagulants are directly compared, PACl performs better at the lower pH, while FeCl removes more viruses at the higher investigated pH. The first observation may be explained by the fact that PACl is operated close to its performance optimum for NOM removal at a pH of 5.5, which can be found in the range from 5.5 to 6.0,[13] while FeCl was operated at a pH of 5.0 and, thus, further away from its performance optimum, which is found at pH values around 4.5 and below. At a pH of 6.5 FeCl performs better, especially at the lower investigated coagulant dosage. There, the virus removal with PACl collapsed to an average of 0.8 log units, while it was similar for the higher investigated coagulant dosage. The PACl dosage of 2 mg Al/L may be in the range of a minimum effective dosage for the given NOM and virus concentrations. At such dosage coagulation is possibly incomplete. However, at a similar molar dosage, FeCl is still performing well. This may indicate a different coagulation mechanism for both coagulants, were FeCl is still active at lower concentrations. This phenomenon has not been investigated further in this study.

It could be generally assumed that at the given experimental conditions PACl has an advantage compared to FeCl since it is preploymerized. Thus, the active polyaluminum species are readily available and no extensive hydrolysis reactions are necessary, as it is the case for FeCl. Coagulation of NOM takes place almost instantly for PACl.[15] Extending the flocculation time starting from 10 s did not significantly improve the removal in that study. It is believed that the coagulation of viruses follows the same principle. This may be especially important since the hydraulic retention time in the pipe flocculator is with 40 s very short. At such conditions no extensive floc growth is possible. However, aggregates formed are big enough to be retained by the membrane. Nonpolymerized coagulants may need more time for their coagulation reactions and the following floc growth.[32]

The infective virus concentration in the permeate decreased slightly over time in most of the experiments, suggesting the formation of a cake layer or pore constriction by complexes consisting of NOM, virus particles and coagulation hydrolysis products enhancing virus removal. Such phenomena have been described, for example, for a kaolinite cake layer, which significantly alleviated MS2 removal with progressed membrane fouling.[26] Turbidity and biomass contained in the raw water may lead to similar observations.[27] Other researchers attributed improved virus removal to irreversible membrane fouling,[33] which maintained virus removal higher even after hydraulic backwashing. However, the gathered data are not sufficient to explain the obtained removal increase over time sufficiently and further, more specific investigations need to be done.

At the lower pH conditions investigated for both coagulants, a removal of at least 4-log units of viruses for both tested coagulant dosages was observed, with the exception of iron chloride after 20 min filtration time and a dosage of 4 mg Fe/L where only 3.3 log units of viruses were removed. These conditions therefore fulfilled both the Norwegian and American requirements for consideration as hygienic barrier. At the higher coagulation pH of 6.5 only FeCl at a dosage of 8 mg Fe/L was close to achieving a 4-log reduction. FeCl at the lower dosage of 4 mg Fe/L and PACl at the higher dosage of 4 mg Al/L achieved only a 3-log reduction, which is at least equal to the 3 log-credits suggested for that process. At a low dosage and at high coagulation pH, PACl failed to comply with any guidelines with poor virus removal below 1 log.

Effect of Coagulation Setup on MS2 Removal. After investigating the influence of coagulant dose and pH value, the conditions showing the highest MS2 removal were chosen for a comparison of an inline coagulation pretreatmet with a conventional tank coagulation setup. Experiments were carried out at pH 5.0, and a coagulant dose of 4 mg/L for PACl, and a pH of 5.5 together with a metal dose of 8 mg/L for FeCl. As shown in Figure 5, rapid inline coagulation with 40s flocculation time performed overall better than the conventional pretreatment setup. The virus concentration in permeate was below 1 pfu/L for PACl in 5 from 6 samples (indicated by an arrow in the figure). This was not the case for the samples taken after 20 min using the conventional setup. With FeCl a clear difference was seen between the two treatment configurations tested. Virus removal was almost complete with the inline pretreatment, whereas it was in the range of 6 to7 log units for the conventional setup. It should be noted that the virus removal with FeCl was 2 log units higher than observed in the experiments comparing different pH values and coagulant dosages (Figure 4a). This is probably due to the higher virus concentrations in the raw water in the first set of experiments ($1 \cdot 10^8$ pfu/mL), compared to a concentration of $6 \cdot 10^7$ pfu/mL in this series. Results from the comparison study show full compliancy with the requirements for hygienic barriers of the coagulation/ceramic MF treatment scheme.

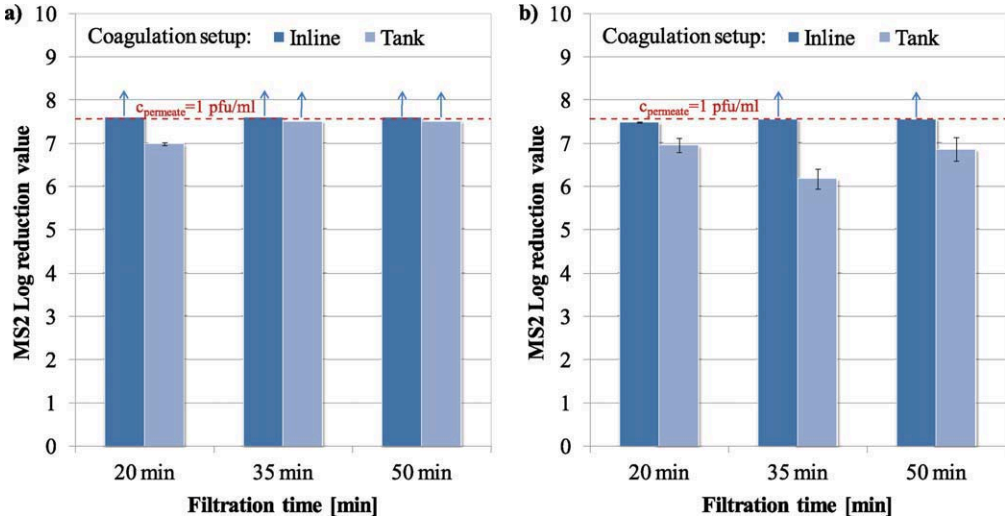

Figure 5. MS2 removal at optimized conditions in dependence on the pretreatment setup and coagulant type (a) polyaluminum chloride (4 mg Al/L, pH 5.5), and (b) iron chloride (8 mg Fe/L, pH 5.0).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The disadvantageous performance of the conventional setup observed is probably a result of the fact that the flocs formed in the slow mixing tank are destroyed in the membrane feeding pump. This might liberate viruses to some extent and even though floc regrowth occurs, it is not as efficient in binding viruses again as the initial coagulation process. A possible higher inactivation of viruses by metallic coagulants due to the significantly higher contact time in the conventional setup was not observed.

Nevertheless, under optimized conditions MS2 viruses are efficiently removed by both process configurations compared. With regard to a technical and economical assessment this indicates that there is no need for sophisticated pretreatment in a coagulation/flocculation coupled with MF filtration process for producing potable water from surface waters containing high NOM concentrations. A simple inline coagulation and flocculation setup is demonstrated to ensure good virus removal if the conditions are optimized, and an enhanced coagulation time does not necessarily improve virus removal. This has been also reported for PACl by others, where HRT's of 1.1, 2.4 and 60 s were investigated and an increase in time only had a minor effect on the MS2 removal.[17] The results from this study confirm that this applies for FeCl as well.

Virus Inactivation by Metal Based Coagulants. To gain more knowledge about the inactivation by metal coagulants, jar test experiments were performed, applying again the indentified optimal conditions for NOM and virus removal. Both coagulants showed an inactivation potential of 1–1.6 log units already after 5 min of contact time as shown in Figure 6a, increasing further up to almost 2 log units or 99% after 60 min. Inactivation potential was found to be larger with FeCl compared to PACl. However, after 60 min both coagulants showed almost the same inactivation potential. Control experiments without coagulant addition did not show any reduction of viable and active virus.

The up to 2 log units of inactivation found in this study correspond to results presented in the literature, where a bit more than 2 log units of virus inactivation was reported, after 60 min by a PACl dosage of 1 mg AL/L in ultrapure water.[19] There, a rapid inactivation was observed at the beginning of the experiment as also found in this study, followed by reduced inactivation during the rest of the experiment. MS2 inactivation rates of 1.0–1.3 log units have been found for a PACl dose of 3 mg Al/L (coagulation pH 7.0), and 1.4 to 1.6 log units for a dose of 5 mg Al/L (coagulation pH 6.7), using a raw water based on tap water with a TOC of 2.5 mg/L and an alkalinity of 0.9 mM.[10] In contrast, no statistical relevant virus inactivation was shown elsewhere, after 3.5 h contact time in an artificial raw water containing $NaHCO_3$ and $CaCl_2$ after adding iron chloride (5 and 10 mg Fe/L, pH6.3, 120 mg/L insoluble silica), and alum (1 and 5 mg Al/L, pH 7.0, no silica addition).[14] Even though the inactivation results obtained correspond well with Matsui et al.[19], the coagulant dose used in this study was significantly higher but achieved inactivation in the same range. This can be explained again by the relatively high NOM content in our raw water, causing a competition among virus particles and NOM molecules for binding sites at hydrolyzed coagulant, a phenomenon also described by Matsui and coworkers.[19] They further reported highest virucidal activity for PACl already at low dosages, possibly due to its prepolymerized character compared to other aluminum based coagulants. However, this study showed that iron chloride has at least the same if not a higher inactivation capacity.

In a second series of jar tests the reversibility potential of inactivation by FeCl was investigated. Two possible methods were examined, destruction of formed flocks by pH increase up to 10 and application of additional shear force by intensive sample vortexing. Compared to the experiments carried out according to the normal experimental protocol, without additional shear and at a pH of 5, both the introduction of additional shear and the increase of pH led to lower virus log reduction of 1.1–1.3 (Figure 6b). It was, therefore, concluded that viruses which are rendered inactive by coagulation, for example, due to adsorption of coagulant or to flocs, can be desorbed to a large extend and are infective again. However, more than 90% of the viruses were still not able to infect a host anymore, despite the reactivation found. This finding does not imply that these inactivated viruses are surely decomposed.

Results found in this study that both shear or pH-increase can restore virus infectivity to a small extent, do not

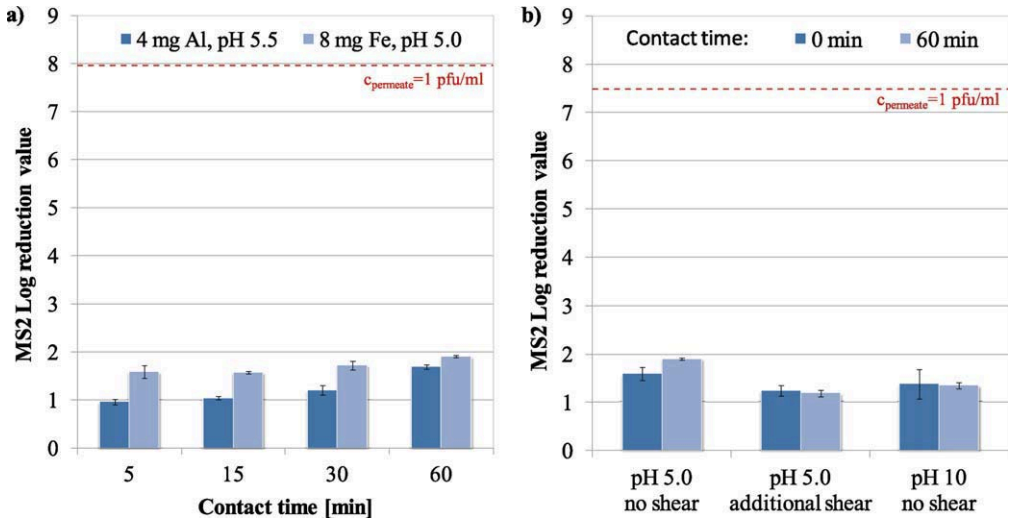

Figure 6. Inactivation of MS2 (a) by PACl and FeCl at optimized coagulation conditions (n = 3), and (b) Inactivation change by FeCl (8 mg Fe/L) in dependence on pH increase or additional shear force (n = 2).

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correspond to findings of other authors, who showed no alleviated infectivity after dissolving the formed flocs by vortexing after adding an alkaline solution (sodium hydroxide + 6% beef extract), and, thus, increasing the pH to 9.5.[19] However, the true inactivation mechanisms remain unclear. Various studies have proposed that hydrolysis products adsorb to the virus surface, alter the morphology of the coat proteins and render them nonfunctional or shield them.[10,18,19,29] In this study the high NOM content in the raw water might play a role. Even though it does not show any inactivation potential by itself, it may contribute to the effect in combination with coagulant hydrolysis products.

Organic Matter Removal. Parallel to the MS2 reduction NOM removal by the inline coagulation configuration was monitored, which increased both with increased coagulant dosage and decreased pH value for both coagulants applied. At lower pH values positively charged metal hydrolysis products can interact with organic matter with a high-negative net charge.[35] PACl removed between 47 and 66% of DOC as shown in Figure 7a), whereas DOC removal with FeCl was in the range of 43–70% (Figure 7b). These rates are 5 to 10% lower than reported in the literature,[13] despite a higher DOC concentration of 5.2 mg/L in the raw water.

Direct comparison of the two coagulants, which were applied at the same molar dosage, showed similar DOC removal rates. At pH 6.5, PACl gave a 5% better DOC removal, indicating an advantage for prepolymerized coagulants compared to nonpolymerized. However, at the lower pH tested for each coagulant, FeCl performed 3 to 6% better compared to PACl.

Color removal, expressed as VIS_{436} reduction, followed the same pattern as DOC removal, but with higher removal rates (Figure 8). PACl removed between 78 and 94%, whereas the removal was in the range of 73–96% with FeCl. UV_{254} absorption was reduced by 58 to 83% with PACl and 43 to 88% with FeCl, respectively. These rates are lower than the ones observed for color removal, but higher than the DOC removal rates. Higher molecular weight,

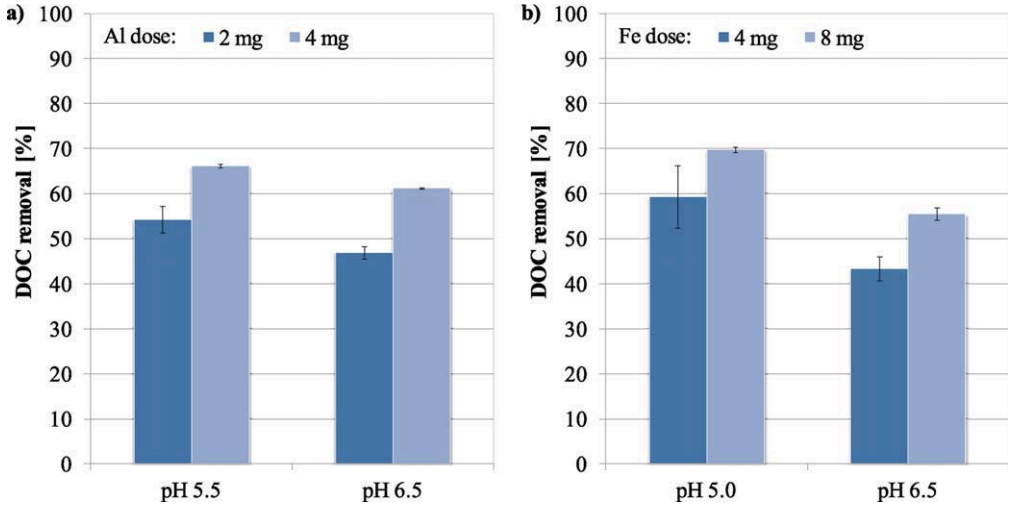

Figure 7. DOC removal with inline coagulation as a function of pH value and coagulant dose with (a) PACl, and (b) FeCl.

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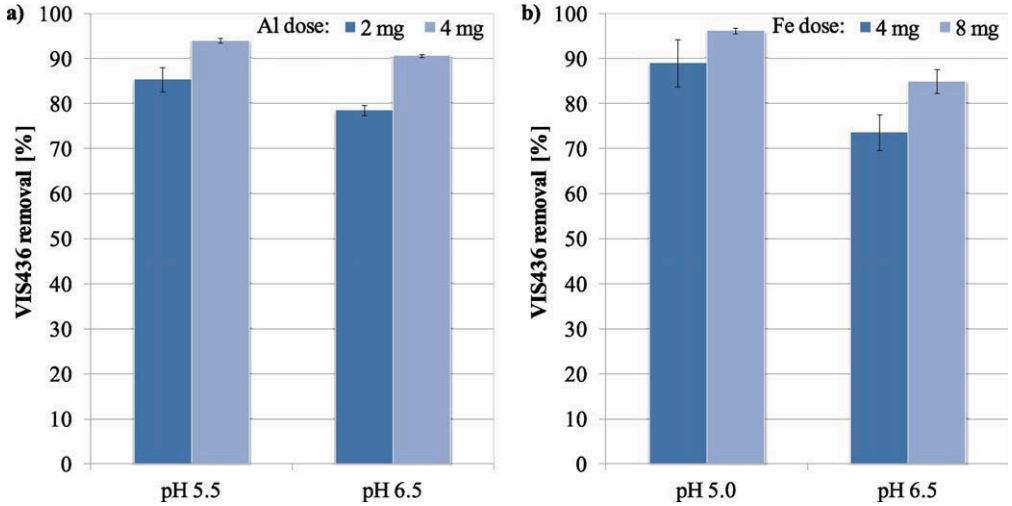

Figure 8. VIS_{436} removal with inline coagulation in dependence on pH value and coagulant dose with (a) PACl, and (b) FeCl.

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hydrophobic NOM, containing a lot of aromatic carbon, is preferentially removed, giving the higher removal rates of VIS_{436} and UV_{254} compared to the total DOC.

Investigations of the influence of the coagulation pretreatment at a given pH and coagulant dose revealed that removal of NOM is independent of the process configuration. Coagulant dosing before the membrane feeding pump followed by 40 s of flocculation showed the same results as 20 min tank coagulation/flocculation. Around 67% of DOC and 95% of color were removed at a coagulation pH of 5.5 and a PACl dose of 4 mg Al/L, independent from the pretreatment. For FeCl, 69% of DOC and 96% of the color were removed at a dosage of 8 mg Fe/L and a pH of 5.0. It can be, therefore, concluded that already after a few seconds of flocculation time particles are created that can be efficiently retained by the membrane. However, membrane fouling was not monitored in this study, which ultimately will affect optimal operating conditions and design criteria for full-scale operation of such a treatment plant. For NOM removal, PACl and FeCl showed comparable results at the same molar dose and at optimal pH value.

Residual Metal. At optimal pH values for NOM removal high-residual metal concentrations were observed, where a higher coagulant dose resulted in twice as high metal residues (Figure 9). With a dosage of 2 mg Al a residual metal concentration of 98 μg Al/L was observed and with 4 mg Al/L 204 μg Al, respectively, at coagulation pH of 5.5. Coagulation with FeCl at pH 5.0 gave residual iron concentrations of 222 μg/L at a coagulant dose of 4 mg and up to 394 μg/L at a dosage of 8 mg Fe/L. At a higher pH value of 6.5, residual metal concentrations well below 150 μg Me/L, the limiting value in the Norwegian drinking water guidelines, were accomplished with both coagulants. Based on the results presented in this study together with earlier findings[13] it can be concluded that optimal conditions for virus and NOM removal cannot be directly applied in practice, since residual metal concentrations will exceed the legal threshold. Therefore, the coagulant dose has to be reduced or the pH

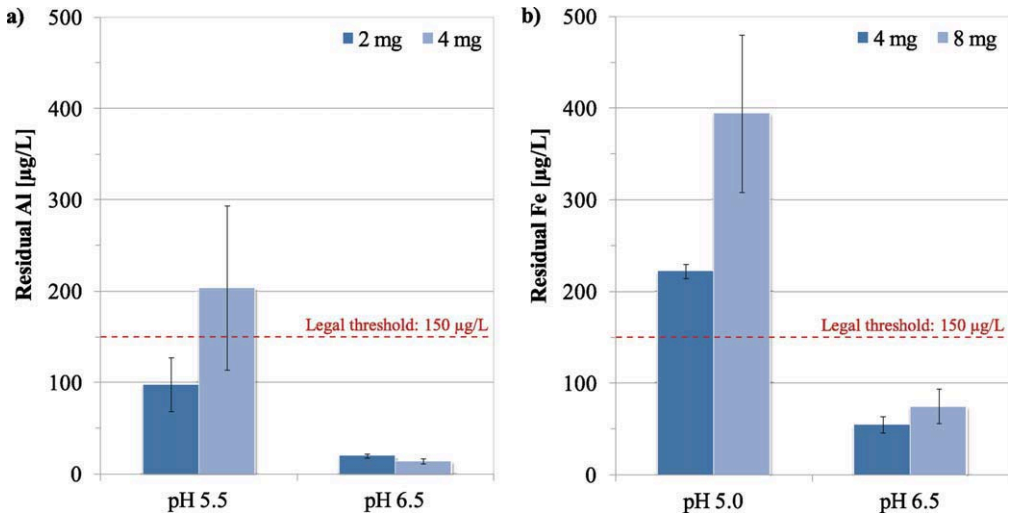

Figure 9. Residual metal concentration with inline coagulation in dependence on pH value and coagulant dose with (a) PACl, and (b) FeCl.

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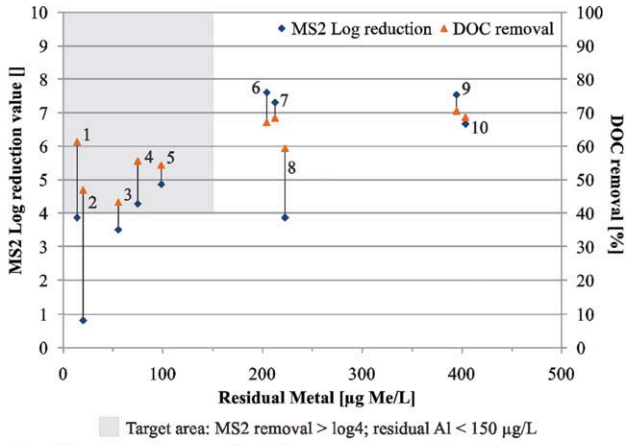

Figure 10. Overall summary of MS2 and DOC removal results.

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value increased. The minimum applicable coagulation pH to comply with residual metal concentrations, at optimized coagulant dose, is estimated to be around 6 for both tested coagulants. It should be noted that PACl produces lower residual metal concentrations compared to FeCl. This conclusion, however, is only surly valid at a coagulation pH of 6.5, where both coagulants were tested.

Comparison of the influence of coagulation pretreatment on the residual metal concentration at optimized conditions for virus and NOM removal revealed no significant difference for both pretreatment setups and both coagulants. With a PACl dose of 4 mg Al/L at a coagulation pH 5.5 the residual metal concentration was found to be 204 $\pm$ 90 μg Al/L using the inline setup, compared to 212 $\pm$ 24 μg Al/L with the tank coagulation pretreatment. At a FeCl dosage of 8 mg Fe/L, 394 $\pm$ 86 μg Fe/L have been found using the inline setup and 403 $\pm$ 46 μg Fe/L for the tank pretreatment, respectively. However, residual metal values exceeded by far the legal threshold of 150 μg Me/L due to a low pH value, which appears to be the major guiding value for the residual metal concentration. Longer flocculation of up to 20 min as used in the conventional coagulation pretreatment is not able to lower the metal residues in the permeate significantly.

Overall Performance. A summary of the results from the investigations in this study are presented in Figure 10. All virus and DOC removal results are shown with respect to associated residual metal concentrations. The gray area in Figure 10 represents the target area of operation, where virus removal is higher than 4 log units (as demanded by the EPA), and the residual metal concentration is below the legal limit (as demanded by Norwegian regulations). As can be clearly seen, only two tests conditions are within this area. Several operating conditions comply with $>$ 4 log virus removal, but failed to meet residual metal limits. Applying a log 3 removal credit as suggested by the Norwegian national association of water and wastewater works for coagulation coupled with UF/MF filtration, more operating conditions comply with regulations. The results from this study can, therefore, be used as a starting point to set recommended operating conditions for a coagulation/flocculation pretreatment coupled with ceramic MF filtration in practice. The coagulation pH needs to be higher than 6 to avoid high-residual metal concentrations in permeate. In this pH region efficient virus and DOC removal can be achieved, however, a higher coagulant dose is required.

Direct comparison of virus and NOM removal indicated similar removal trends (Figure 11). It increased for both components with increased coagulant dosage and decreased pH value. High DOC removal implied also high MS2 removal. This behavior may indicate similar coagulation mechanisms. Both, MS2 viruses and NOM molecules are negatively charged in the investigated pH range. As a result they can both react in a similar way with provided coagulant. Since the removal increases at lower pH, it is suggested that the reaction with positively charged metal complexes is the dominating removal mechanism for both. Thus, enough coagulant has to be dosed to ensure efficient virus removal if waters with a high content of NOM are treated by coagulation.

Conclusions

While only up to 1 log unit of MS2 bacteriophages was removed by ceramic MF itself from a feed solution with high NOM content, the retention increased drastically if coagulation pretreatment was applied. Lowering the coagulant pH from 6.5 to 5.5 for PACl and 5.0 for FeCl, respectively, and doubling of the coagulant dose from 2 to 4 mg Al/L and from 4 to 8 mg Fe/L, respectively, maximized the virus removal, resulting in more than 6 log unit reductions up to complete virus retention.

Comparison of an inline coagulation and rapid flocculation (45 s HRT) with a conventional rapid and slow mixing tank pretreatment (20 min) showed a similar performance for the simpler inline process configuration. The tank coagulation/flocculation configuration, however, showed a 1 log unit less virus removal, probably due to flock destruction and virus

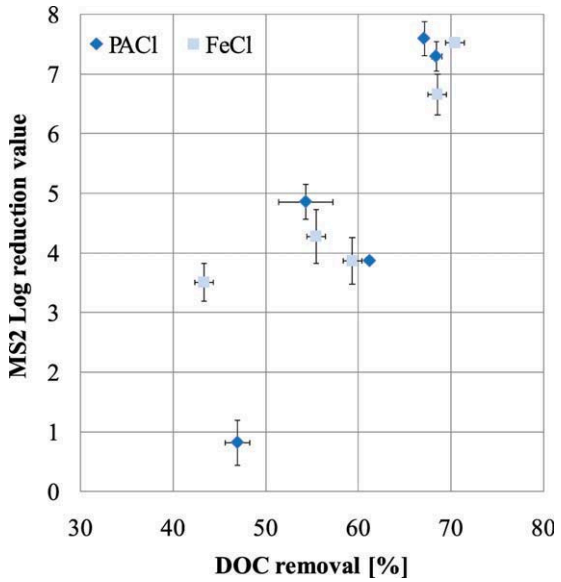

Figure 11. Direct comparison of MS2 and DOC removal.

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liberation in the membrane feeding pump. The flocculation parameters pH and coagulant dose had a much more significant influence on virus and NOM removal. Both, PACl and FeCl, are able to efficiently remove viruses and showed a balanced performance. While FeCl removed 1 to 2 more log units of MS2 at pH 6.5, PACl showed a slight advantage at the lower optimal pH.

In contrast to literature findings, 2 to 4 times higher coagulant dosages were necessary to accomplish similarly high-virus removal rates. This was explained by the high NOM concentration in the feedwater, which like the virus particles is negatively charged at the applied coagulant pH values and, thus, reacts very well with the hydrolyzed coagulant. High NOM in the raw water diminishes free coagulant and is in directed competition with the virus particles.

Virus removal was observed to improve over time for the tests done in this study. This suggests that the removal properties of the membrane change during filtration, most likely due to development of a cake layer on the membrane surface consisting of coagulated natural organic matter molecules and virus particles, or pore constriction by these substances.

Virus inactivation by metal coagulants reported in the literature was confirmed. Both applied coagulants showed virus inactivation of a little less than 2 log units after 60 min contact time. That is equivalent to a virus inactivation of 99%. Inactivation was observed to increase rapidly at the beginning of an experiment and continued with a reduced rate. The inactivation was only reversible to a small extent by applying a shear force or dissolving the flocks at pH 10. Infectivity was increased by 0.6 to 0.7 log units.

NOM and virus removal followed a similar pattern. It increased with increasing coagulant dose, decreasing coagulation pH, and was independent of the pretreatment setup. Color was preferentially removed to DOC.

At high-coagulation pH, the residual metal concentration was well below the legal limit of 150 μg/L and, therefore, not an issue for neither of the two coagulants. At the lower pH values, found to be optimal for virus and NOM removal, the residual metal increased drastically and reached up to 4 times the legal limit in some experiments, particularly at higher coagulant dosages. The residual metal is, therefore, a limiting factor for selecting the conditions for operation in practice, where coagulation pH values need to be chosen that meet required residual metal concentration in the permeate.

For compliance with legal regulations, coagulation pH values should be set at 6 or higher to avoid high-residual metal concentrations. At these pH values efficient virus removal can still be achieved, however, higher coagulant dosages are required. By optimizing the coagulation/flocculation pretreatment, efficient removal of NOM can be achieved while complying with hygienic barrier requirements, resulting in virus removal of 4 log units and higher. Coagulation/flocculation pretreatment coupled with ceramic MF filtration, is, thus, a viable and flexible treatment scheme for the production of high-quality potable water from surface waters with high NOM concentrations.

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