Significance of flocculation for NOM removal by coagulation–ceramic membrane microfiltration

T. Meyn, A. Bahn and T. O. Leiknes

ABSTRACT

Potable water treatment with coupling coagulation–microfiltration processes are still rarely applied in commercial treatment plants. Raw water with a high content of organic matter, typical for Norwegian surface water sources, was treated in this study using a ceramic microfiltration membrane system. Three different pre-treatment options were investigated, a classical two-stage flocculation, a simplified one-stage fast mixing step and an inline flocculation treatment, using an iron chloride coagulant. DOC removal was similar (76–81%, 5.5 mg C/L in raw water) in all compared setups. The more compact, energy efficient inline configuration was investigated further, varying flux (140 and 220 LMH), pH (4.5, 5.5 & 6.5), G-value (60 and 300 s⁻¹) and HRT in the pipe (7 and 30 s), while monitoring DOC removal, fouling rate and residual iron concentrations. DOC removal was strongly pH dependent; 70% at pH 4.5, and 47% at pH 6.5. At high flux of 220 LMH the membrane fouled quickly and sustainable operation was not possible. At 140 LMH fouling was much less and no severe fouling was observed during the experimental period. Residual metal concentration was found to be the limiting parameter in the design and operation of the process configuration. Metal concentrations below the regulation limits (200 μgFe/L) were only achieved at pH 6.5. Reversible fouling was only observed at higher pH values.

Key words | ceramic membranes, drinking water, flocculation, microfiltration, natural organic matter

INTRODUCTION

Production of potable water from surface water sources can be a challenge due to many factors. Climatic and geographical conditions have given Norway an abundance of water resources and about 90% of drinking water supplies in Norway are from surface water, mostly lakes with very low turbidity. One of the major problems of using these surface waters in northern climates is high content of natural organic matter (NOM), resulting in high colour and total organic carbon (TOC) concentrations. Even though NOM is generally not harmful itself, removal of NOM is required since coloured water is unattractive to consumers, results in colouring of clothes during washing, can cause odour and taste, increases corrosion and biofilm growth in the distribution network, and is a precursor to the formation of disinfection by-products (DBP) when water is disinfected. NOM also forms complexes with heavy metals and organic micro-pollutants, affects stability and removal of particles and pathogens, and can affect the unit processes in a treatment scheme in various ways (i.e. increased coagulant dosages, sludge production). The use of surface water with high NOM content is also of concern as recent studies have documented a steady increase in the content of NOM in natural waters in Norway over the last 30 years (Forsberg 1992; Ratnaweera et al. 1999; Hongve et al. 2004). This is not unique to Norway, and a need for more efficient removal of NOM and more NOM tolerant treatment technologies is foreseen.
The most common drinking water treatment plant designs in Norway are based on coagulation and direct filtration or nanofiltration (NF) membrane filtration processes. Coagulation direct filtration plants (enhanced coagulation) are still the dominant treatment plant design option, however, in the last 15 years membrane processes based on NF spiral wound module configurations have been successfully used, with approximately 100 plants in operation today. Alternative treatment schemes to these options are the use of microfiltration (MF) and ultrafiltration (UF) membranes, using alternative membrane module designs (i.e. hollow fibre cross-flow modules, submerged modules). Studies are also found that report and demonstrate the advantages and benefits of combining coagulation pretreatment with membrane filtration when UF and MF membranes are used (Ødegaard et al. 1999, 2000). Pretreatment by coagulation has been reported to be a potential strategy to reduce and control fouling, an inherent challenge in all membrane processes. Common for all of these studies are that they are based on polymeric membranes (Lahoussine-Turcaud et al. 1990; Peuchot & Ben Aim 1992; Lebeau et al. 1998; Schäfer et al. 2000; Kim et al. 2001; Machenbach et al. 2002). The more energy efficient, low pressure MF/UF membrane plant configurations also appear to be the preferred solution. Due to their physical properties, mechanical stability and resistance against chemicals, there is an increasing interest in using inorganic ceramic membranes for NOM removal (Weber et al. 2003; Lee & Cho 2004; Leiknes et al. 2004). The effect of higher investment costs of ceramic compared to membranes can be diminished by operating ceramic membranes with higher fluxes and by achieving good membrane fouling control/mitigation. In an ongoing study, the combination of ceramic microfiltration with coagulation/flocculation pretreatment has been investigated for typical Norwegian surface water treatment and it has been demonstrated that high DOC and colour removals using iron chloride and polyaluminium chloride as coagulants, operating at optimal dose and pH conditions, can be achieved (Meyn et al. in press). Results show that DOC and colour removal can be achieved at relatively low coagulant dosages, however, this strongly depends on the coagulation pH and good flocculation conditions.

In this study the significance of flocculation on NOM removal for a coagulation/flocculation and ceramic microfiltration treatment scheme was investigated. The aim of the study was to investigate various modes of flocculation on NOM removal and to investigate the influence of operating parameters such as coagulant dose, pH-value, G-value on the flocculation step and how this affects the overall performance of the membrane filtration process.

**METHODS**

**Raw water production**

The raw water for all conducted experiments 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 representative for typical Norwegian raw water sources (Machenbach et al. 2002; Leiknes et al. 2004; Meyn et al. in press). The analogue feed composition consisted of water with a colour of 50 ± 1.13 mg/L Pt at pH 7, UV254-adsorbance of 24.6 ± 0.8 m⁻¹ and DOC concentration of 5.5 ± 0.3 mg/L C.

**Pilot plant**

A coagulation/flocculation membrane filtration pilot plant supplied by NGK, Japan, was applied in this study. It contains three independent controllable process trains thereby allowing different flocculation modes and operating conditions to be investigated in parallel. The chosen options investigated consisted of a classical two-stage flocculation with a fast mixing tank followed by a slow mixing tank, a simplified one-stage flocculation with a fast mixing tank, and a simplified inline pipe flocculation device. Figure 1 shows a schematic of the experimental setup—A: classical two-tank and one-tank process configuration, B: simplified inline pipe flocculation device. In the last design, a pipe flocculator followed the feed pump to the membrane filtration unit. In this mode the feed pump was also utilized as the mixing device for adding the coagulant.

In this study, multi-channel ceramic membranes operated in dead-end/inside-out mode with a nominal pore size of 0.1 μm were used. Each module has 55 channels, a length of 1.0 m, giving an effective area of 0.45 m². The membrane module is closed at one end (dead-end operation) and feed
water is pumped into the membrane in an up-flow direction, operated in constant flux mode. Backwashing was performed with permeate after a filtration cycle of 1 hour (Table 1). During the backwashing process, the backwash water storage tank is pressurised (500 kPa) and permeate is pushed in reverse through the membrane, followed by a short blast of pressurised air (200 kPa) at the top of the module, the whole procedure taking about 10 seconds. Between each experiment the membrane modules were cleaned intensively using a chemical cleaning protocol based on soaking the membrane in citric acid solution (1%) and then sodium hypochlorite solution (3 mg/L). Clean water permeability was measured to verify removal of all foulants after cleaning and to ensure the same starting conditions for all tests. The permeability was fully restored after each enhanced chemical cleaning.

Table 1 | Membrane module specifications

<table>
<thead>
<tr>
<th>Type</th>
<th>Ceramic MF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length [m]</td>
<td>1</td>
</tr>
<tr>
<td>Module diameter [m]</td>
<td>0.03</td>
</tr>
<tr>
<td>Channels per module</td>
<td>55</td>
</tr>
<tr>
<td>Channel diameter [mm]</td>
<td>2.5</td>
</tr>
<tr>
<td>Module area [m²]</td>
<td>0.43</td>
</tr>
<tr>
<td>Nominal pore size [µm]</td>
<td>0.1</td>
</tr>
<tr>
<td>Backwash intervals [h]</td>
<td>1</td>
</tr>
<tr>
<td>Backwash procedure/pressure [bar]</td>
<td>Filtrate at 5 bar and air at 2 bar</td>
</tr>
</tbody>
</table>

Experimental conditions

A parametric study was performed for the simplified inline setup, investigating the influence of the flocculation parameters pH value, HRT and G-value in the pipe flocculator on the process parameters DOC removal, residual metal concentration and membrane fouling. Different pipe flocculators were used, tubes of different length and diameter, to obtain varying retention times and G-values depending on the experimental conditions desired. This was investigated for two flow rates, 1.0 and 1.6 L/min, corresponding to membrane fluxes of 140 and 220 LMH respectively. An iron chloride coagulant (PIX-111, Kemira Chemicals) was used, constant dose of 6 mg Fe/L, for all experiments conducted.

Table 2 gives an overview of the combinations of operating conditions tested. For one experiment all three trains were set up with the same experimental conditions except for pH, which was set at 4.5, 5.5 and 6.5 respectively. To exclude potential bias by train or membrane module specifics, distribution of parameters between the three trains was randomized. Each experimental run was terminated when TMP exceeded 200 kPa or a set maximum operating time of 96 hours was reached.

Experimental analysis

Analytical equipment/instruments

Membrane performance was monitored by logging the TMP development for constant flux operation over time.
Water samples were taken before the coagulant dosage point, the feed water to the membrane and of the permeate twice a day during different stages in the process cycles. Turbidity measurements (90° scattered light method, Turbidimeter 2100N, Hach) and the residual metal concentration (measured by High Resolution ICP-MS) in the permeate were analysed for each sample. The removal of organic matter was monitored online by measuring colour, UV-adsorption at 254 and 436 nm and DOC (Spectrolyser®, s::can Meßtechnik GmbH, Vienna, Austria).

**Presentation of results**

Obtained results were visualized in effect plots and interaction plots. The effect plot is a plot of means of a response, i.e. the residual DOC concentration in the permeate at each level of a factor, i.e. pH value. Plots give a general idea of which effects may be important and which can be neglected. To construct such a plot, all obtained results are grouped in dependence on the level of the plotted factor, i.e. if obtained at high or low pH, and averaged. The horizontal line represents the grand mean, which means the average of all observations of the plotted response. All plots within one diagram have the same magnitude, making the influence of different factors on the same response comparable. An effect occurs when the mean response changes across the levels of a factor. Effect plots cannot be interpreted separately from interaction plots, because some effects only occur at a single condition, but are intensive enough to dominate the overall average. An interaction takes place when the effect of one factor depends on the level of another factor. It occurs when the change in response from the low level to the high level of one factor is not the same as the change in response at the same two levels of a second factor. This can be visualized in interaction plots. Parallel lines in a plot symbolize no interaction. The greater the difference in slope between the lines, the higher is the interaction. Each row of windows in the plot illustrates the impact of a certain parameter. Results from the study are predominantly presented in this manor.

**Evaluation of fouling rate**

In this study measurements were conducted to distinguish between reversible and irreversible fouling. By definition, reversible fouling can be removed by normal backwashing procedures whereas irreversible fouling has to be removed by enhanced chemical cleaning when a defined level for the system is reached. The TMP for each cycle before and after a backwash was measured, where the area difference between the two curves is defined as reversible fouling (see Figure 4). To quantify the actual amount of fouling, or fouling rate, TMP curves measured were approximated by the exponential function:

$$\text{TMP} = R_0 e^{kV}$$

where $R_0$ represents the initial TMP and $k$ the fouling rate. The fouling rate $k$ of the irreversible fouling curves were then used for the overall fouling rate evaluation in relation to the different applied flocculation conditions and subsequently compared to each other.

To check the quality of the exponential approximation used in the data analysis, the difference of the TMP measured after filtering a volume of 4,000 L compared to
the initial TMP at the start of the experiment was calculated
and compared to the ones calculated with the model.
Measured and predicted values showed a good linear
correlation, and it was, therefore assumed that the
expression in equation 1 was a suitable approximation to
determine the fouling rates measured is this study for the
various operating conditions tested. To assess the amount of
reversible fouling the area under both, the reversible and
irreversible fouling curves was calculated with help of
exponential approximation and the area difference
calculated.

**RESULTS AND DISCUSSION**

**Assessment of the three treatment trains**

Three options were chosen as alternatives to apply the
cozagulation and flocculation stages in the treatment process
and investigated under similar conditions. The aim of the
evaluation was to assess the significance of the flocculation
step for the overall performance of the treatment scheme,
i.e. DOC removal efficiency and membrane filtration fouling
rates. A classical two-stage flocculation unit was compared
to a simplified one-stage flocculation, and with an inline
pipe flocculation. The two-stage treatment train included a
rapid mixing reactor (193 rpm) with a hydraulic retention
time (HRT) of 6.7 minutes, followed by a slow mixing tank
(53 rpm) with a HRT of 13.3 minutes, in total 20 minutes.
The one-stage flocculation included only the fast mixing
stage, HRT 6.8 minutes, before feeding the water to the
membrane filtration unit. The pipe flocculator was operated
with a G-value around 7.5s and HRT of 0.75 minutes. All
three flocculation setups gave similar DOC
removal efficiencies (76–81%), although the HRT within
the respective flocculation steps was significantly different
(0.75 – 20 min). Overall results are illustrated in Figure 2.

Based on the results observed it may appear as though
flocculation is not a significant operating parameter for
efficient removal of DOC under the conditions tested. In
addition, the use of an inline pipe flocculator potentially
represents a more compact treatment plant with fewer unit
processes, simpler to operate and thus requiring less energy.
Further studies were therefore conducted to evaluate the
significance of flocculation in the treatment scheme and to
assess the applicability of an inline unit with respect to
process performance. The following discussion of results is
based on this assessment.

**Inline flocculation – membrane fouling**

Fouling of the membrane was found to be strongly flux
dependent. Operating with a flow rate of 1.6 L/min,
(corresponding flux 220 LMH), the membrane was severely
fouled after a small filtration volume due to the higher load
of the membrane. Another reason for this could be that
during all the experiments a constant backwash interval
of 1 hour was applied, thus, at the higher flow rate the
membrane was backwashed after filtration of 100 L water
compared to 60 L at the low flow rate. The higher flow rate
might also cause a denser cake. Fouling was less pro-
nounced depending on the applied coagulation conditions,
but overall too strong to consider this flux for a sustainable
process operation. Most of the experiments had to be
stopped before the set target volume of 4,000 L was filtered,
with only one experiment continuing until 7,000 L. As
expected, operating at the lower flux of 140 LMH, the
membrane showed much better performance (i.e. less
fouling) and it was possible to run the experiments much
longer before fouling development became too severe. In all
cases operating with a flux of 140 LMH a total filtered
volume in excess of 7,000 L was achieved. Subsequently, for
the two fluxes chosen, fouling rates observed at 140 LMH
were much lower compared to 220 LMH (Figure 3). For the
evaluation of results, TMP development was related to the permeate volume to derive the fouling rate and not to filtration time, since this would not reflect the higher membrane load after changing from a low to a high flow rate.

In addition to flow rate, pH also had a strong influence on the membrane fouling. Particularly at a pH 5.5 the membrane fouled very quickly, while at the higher and lower pH fouling was less severe. This effect was only observed at the higher applied flow rate of 1.6 L/min (Figure 3) and not at the lower flow rate of 1.0 L/min. As for results for DOC removal, flocculation conditions at the lower flow rate appear to be advantageous since no pH influence on the membrane fouling was found. The high fouling rates measured at high flow and pH 5.5 can possibly be explained by unfavourable changes in floc and cake characteristics. Combining all the negative effects under these operating conditions this phenomenon may be explained by: the higher volume of water filtered during a cycle, the lower retention time in the membrane, and a possibly denser cake due to changed floc properties. The mechanistic change of the coagulation mechanism may be the cause as at pH higher than 6.5 sweep coagulation dominates, and changes to adsorption destabilization below pH 6 for the applied iron dose of 6 mg Fe/L. Interestingly, no special effects were observed at this pH for DOC removal or residual metal results measured.

The retention time and the G-value displayed only a minor influence on the membrane performance, however, the influence was slightly more pronounced for the higher flow rate applied. A lower G-value and retention time appear to be slightly more beneficial for the membrane performance in this case. From the interaction plot in Figure 3, it is apparent that both G-value and retention time have a higher influence on membrane fouling at pH 6.5. This might indicate that under sweep coagulation conditions these parameters have a higher influence than on destabilization conditions. At this pH the flocs possibly become smaller at a higher G-value and build up a denser cake, whereas during adsorption destabilization conditions the flocs are smaller anyway and are not changed very much by the set up flocculation conditions.

A strong correlation between the amount of reversible fouling and the applied pH was measured (Figure 4). With increasing pH a stronger pressure increase during a cycle was observed, whereas the TMP after backwashing, which represents the irreversible fouling expressed by the fouling rate, was more or less constant. This was observed under all applied conditions and is probably due to the different coagulation mechanisms at different pH values. At a pH of 6 more particles and turbidity might be enmeshed due to sweep coagulation, resulting in a good removable but resistance causing cake layer, whereas at lower pH the cake contains more NOM aggregates, forming a denser but thinner cake.

**DOC removal**

Depending in the applied flocculation conditions, between 54 and 63% of DOC was removed from the raw water, feed
concentration 5.8 mg/L DOC. All four investigated factors have a considerable influence on the DOC removal (Figure 5). As shown in further studies, the DOC removal is strongly dependent on the applied pH value (Meyn et al. in press). Best DOC removal was achieved at the lowest applied pH of 4.5 and the lowest removal at pH 6.5. This can be explained by the more efficient reaction of NOM molecules with the iron hydroxocomplexes, which are more stable at lower pH values.

At the higher flow rate more DOC was found in the membrane permeate. Since all the experiments were carried out with two different flow rates but under otherwise same flocculation conditions this difference can only be explained with the changed hydraulic conditions in the membrane channels. Laminar flow conditions can be assumed in the membrane channels for both conditions since the average Reynolds number increases from ca. 150 to 250, which is still in the laminar range. At the lower flow rate of 1.0 L/min (corresponding to flux 140 LMH), the flocs have more time to interact within the membrane where the internal channels induce a kind of pipe flocculation. As reported by Yonekawa et al. (2004), this has a significant effect on the
floc development and the removal performance is substantially improved. Due to a unique flow pattern in the membrane channels micro-particles increase 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 shear-induced lift force. The flocs then form a cake layer at the dead-end points of the membrane. This effect might be reduced by an increased fluid flow in the channels which causes a reduction in residence time and increased turbulence.

Results show that both the retention time and the G-value in the pipe flocculator also have a strong effect on the DOC removal. Lower residual DOC concentrations, and therefore better removal, was measured with a higher retention time and a higher G-value. A longer retention time in the pipe flocculator allows the flocs to have more time for development, which is beneficial for the DOC removal. Applying higher G-values smaller but more stable flocs can be obtained, which then do not get destroyed while entering the membrane and can interact with the membrane surface (Yonekawa et al. 2004).

The interaction plot in Figure 5 reveals a relationship between the flow rate and the retention time. At the higher flow rate of 1.6 L/min (corresponding flux 220 LMH), the retention time does not appear to have any influence on the DOC removal. At the lower flow of 1.0 L/min (corresponding flux 140 LMH) a response can be observed. This might indicate again that flocculation in the membrane plays a very important role in the removal efficiency. Since the hydraulic conditions in the membrane are not changed but the retention time in the membrane is reduced from approximately 16s to 10s, this time decrease may possibly significantly reduce micro-particle growth in the membrane. Subsequently this suggests that coagulation/flocculation before the membrane do not have a large influence on DOC removal in the configuration applied in this study. This implies that as long as enough micro-particles are formed which can grow rapidly inside the membrane channels, efficient removal will take place. This behaviour might be unique to inline flocculation with very short total retention times in the system, as applied in this study. Systems using a classical tank flocculation approach might perform different.

Residual iron concentration

In general, the residual iron concentrations were high for most of the operating conditions tested. For some operating conditions conducted at pH 6.5 a residual iron concentration less than 200 µg Fe/L was measured, which is the limiting value in drinking water regulations in various countries. This parameter was therefore identified as one of the key parameters in choosing and justifying optimal operating conditions for the process combinations tested. Results from the residual iron concentrations are summarized in Figure 6.
Solubility concentrations of metals are a function of pH, and as expected pH was found to influence the residual metal concentration for the iron based coagulant. With decreasing pH the solubility of iron increases. This is also the case in the experiments performed in this study where residual iron concentrations below 200 µg Fe/L were only achieved at pH 6.5. Looking at the overall averaged results (Figure 6), the flow rate does not have any influence on the residual iron concentration, which is expected from a chemical point of view where metal concentration should only be dependent on quality parameters influencing the chemical equilibrium, i.e. component concentration, temperature and pH.

At longer retention times of the fluid in the pipe flocculator higher residual iron concentrations were observed. From the interaction plot, influence of the residence time is biggest at the lower pH values and thus in the pH region there the metal dissolution is expected to be highest. There is also a dependence on the flow rate. At the higher flow rate no influence of the retention time is observed while at the low flow rate a low retention time of 7 s promotes a low residual metal concentration and a higher retention time of 30 s leads to increased metal residues. Since the flow pattern in the pipe flocculator should be the same at both flow rates due to the differently chosen pipe diameters and lengths the origin for this behaviour could be found again in the membrane. It might be possible that the differences of the retention in the membrane previously described may have an influence.

The G-value has just a minor effect. However, at a lower flow rate high G-values are benefitting low residual iron concentrations and at higher flow rates higher G-values respectively.

**CONCLUSIONS**

All three compared treatment configurations showed a good and reliable process performance. DOC removal was efficient, varying from 76.2% (inline setup) to 80.6% (classical 2-tank setup), and with hydraulic retention times in the flocculation varying from 45 seconds to 20 minutes. A more detailed study was conducted for the inline setup as this configuration showed the potential of being simpler, less time consuming and therefore more energy efficient. Dependence on different pH values, hydraulic retention times and G-values in the flocculator was investigated with respect to process performance. Up to 63% DOC removal was achieved and membrane fouling was controllable as a function of the operating conditions tested.

DOC removal strongly depended on the pH value. At the investigated pH 4.5 and 5.5 the removal was greater than at 6.5. However, the residual iron concentration increased similarly making it impractical to operate at these conditions to meet regulation standards (200 µg Fe/L). The residual metal concentration was therefore identified as a key limiting parameter in the design and operation of the tested inline flocculation configuration. Compliance to the residual metal concentration was only achieved at pH 6.5. This problem can probably be solved or reduced by further improvement of the initial mixing conditions. In this study the membrane feed pump was used as initial mixing for coagulant dosing and pH adjustment. An assessment of improved mixing devices is therefore a task for future studies.

A sustainable operation of the process was only achieved for the lower flux (140 LMH) investigated in the process combination applied in this study. The higher flux (220 LMH) gave relative quick and severe membrane fouling, and only minor influence on the membrane fouling was observed for varying G-value and HRT in the pipe flocculator. The amount of reversible fouling strongly depended on the pH. At lower pH almost no reversible fouling was found, whereas at higher pH it was more obvious. Further studies are required to determine the practical operating range and to optimise the process configuration.

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