Description of different effects of in-line coagulation upon semi-dead-end ultrafiltration


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Abstract This paper describes the results of research focussed on the different effects of in-line coagulation (FeCl₃), towards the operation of semi-dead-end UF for drinking water and process water production starting from surface water. In this research, firstly the effects of the use of FeCl₃ on the formed cake were studied, by both direct and indirect measurements. Using the ESEM technique (environmental scanning electron microscopy), which enables one to make pictures of wet samples, we observed that cake thickness was much higher upon use of FeCl₃ (20 instead of 2 µm). As a result, the cake porosity was calculated to be much higher with than without coagulant use (93% instead of 37%). From the stability (non-increasing) of the starting transmembrane pressure (TMP) in the successive filtration cycles, upon semi-dead-end operation, it was concluded that cake layer was less prone to adhere to the membrane surface when using coagulant. This is even more emphasized once the dosing is stopped, as a consequence the TMP rises very steeply under difficult circumstances, such as; high flux rates, high water recovery rates, and the use of membranes made from polymers with high adsorption properties. Secondly, indirect effects of the use of coagulant on filtration behaviour were investigated. Thus, it was found that TMP increase in the filtration cycle was much lower, due to depth filtration in the formed high-volume cake, and TMP was much more stable over a long time. These observations were in good agreement with found higher cake porosity. Moreover, it was observed that due to the use of a coagulant, the influences of membrane polymer nature and membrane structure disappeared, cleaning action could be postponed and cleaning aggressiveness could be lowered. In addition, water recovery and flux rate could be increased, and influence of seasonal water quality variations could be better faced. Finally, it was found that the treatment of surface water with high DOC content (e.g. 10 mg DOC/l) was enabled.

Keywords Drinking water production; in-line coagulation; semi-dead-end; surface water; ultrafiltration

Introduction
From the second half of the 1990s, semi-dead-end ultrafiltration (UF) was implemented on large scale in several projects throughout Europe (Vos et al., 1997; Doyen, 1997; Manth et al., 1998; Kamp et al., 2000), replacing the conventional pre-treatment techniques used in the drinking water industry for clarification and disinfection purposes like: coagulation followed by sedimentation, flocculation, or slow and rapid sand filtration, and multimedia filtration. Nowadays numerous installations have already been constructed. The first realisations, however, were the outcome of a tedious exploratory testing procedure, to establish the most suitable pre-treatment and most optimal operational procedure. The latter were often optimised even after the real installations were commissioned. The origin of this problem lies, due to economical reasons, in the necessity of operation at high fluxes combined with high recoveries. At the time these installations were built, the membrane costs were still at quite high levels (75–100 €/m²), which forced the users to explore the
limits of operation and to find alternative, much easier, operational modes to do so. In our opinion the most important “accidental observation” with this respect was the use of in-line coagulation which was mostly intended (pre-treatment) for improving the removal efficiency of UF membranes for organic molecules (Ruohomäki et al., 1998). It was found that, apart from the increased removal efficiency for organics, membranes could be operated much more stably (Soffer et al., 2000). The experiences varied from no effect, to considerable positive effect.

In this paper some experiments are described enabling the assessment of the direct and in-direct effects of in-line coagulation. The most important study revealing the most important direct effect is the one of the morphology of the formed cake. In this paper interesting ESEM pictures of filtration cakes will be shown explaining partly the more stable operation upon on-line coagulation. Also the different indirect effects of coagulation are highlighted by dead-end experiments.

Results and discussion

Direct measurements of the effects of in-line coagulation on the filtration cakes

In order to study the direct effects of in-line coagulation, filtration cakes formed with in-line dosing of FeCl₃ (0.7 mg Fe³⁺/l) and without dosing, have to be prepared. For this purpose we used a small dead-end “witness” filtration module containing one single tubular membrane, which is placed in parallel with a pilot filtration module in an UF pilot. The used witness membrane was a tubular Stork Friesland membrane, made of PVDF (type WFF 4385) with an internal diameter of 5.2 mm and a length of 42 cm, totalising a surface area of 68.6 cm².

The raw water used for this investigation was originating from Canal Albert water from Grobbendonk (near Antwerp). It contained 12.5 mg of SS per litre on the day of the experiments.

In order to be sure that the witness membrane was fed with a representative feed or coagulant/feed mixture, which is essential to make reliable conclusions regarding the cake properties, the witness module is placed in parallel with the pilot module. The tubular membrane type was chosen as the witness membrane for two reasons. The first one is the facilitated sample isolation/preparation due to the larger diameter. The second is its much higher permeability (= 1,500 l/h.m².bar) than the pilot membrane (X-Flow Norit, 370 l/h.m².bar). This last property is necessary to enable the flux control of the witness membrane just by a needle control-valve at the permeate side. By this way of operation identical flux rates (100 l/h.m²) could be realised on both module types. The flux rate of the witness membrane was measured by using an electronic balance, and the flux of the pilot membrane with a flow meter. The filtration time (or cycle time) for preparing the two different cakes was always one hour. At the end of the filtration time the witness membrane module is immediately removed from the filtration pilot, and the membrane is taken out of the module. Special precautions were taken in order not to modify the so-produced filter cakes.

Environmental scanning electron microscopy (ESEM) was used to study the morphology of the formed filtration cakes. This SEM technique is also referred to as high pressure or low vacuum SEM, and can address uncoated samples that are known to be difficult to image and is applied to easily charged samples. Another area where environmental SEM is particularly applicable is for specimens not compatible with high vacuum used at classical SEM, such as volatile specimens (Kodaka et al., 1992). Since ESEM sampling room requires only a limited vacuum (50–3 Torr at a temperature of 5°C), evaporation of water thus is limited to a minimum. This is also the reason why this microscope is normally used to study “living” organisms. This feature enables us to study wet samples. Hence it can also be used for visualisation of wet membrane filtration cakes under more “real”
conditions. This makes it very useful for our research. Another feature is that surface charging problems experienced in high vacuum SEM are virtually eliminated in the low vacuum SEM, extending imaging capabilities to samples previously difficult to use or incompatible with conventional methods.

Results of FESEM analysis of filter cakes
As already discussed two types of filtration cakes were prepared: one type without, and another with coagulant dosing. Also a non-used membrane was studied as a reference for comparison.

Figure 1 gives an ESEM-view of the top surface of the reference membrane, whereas Figures 2 and 3 show the cross-section and the surface of the cake after one hour of filtration without any dosing. Figures 4 and 5 give a view of cross-section and the surface of the cake after one hour of filtration with 0.7 mg/l of Fe$^{3+}$ (FeCl$_3$) dosing.

Figure 1 was taken at 4.9 Torr with a magnification of 500. From this picture it can be concluded that the unused witness membrane (reference membrane) has a quite smooth top surface. The bar on Figures 1–5 represents 50 µm.

The smooth surface disappears once the membrane has been exposed to filtration with the raw water. From Figures 2–5 it is clear that cake-thickness upon FeCl$_3$ dosing is much bigger than without dosing. The cake layer thickness is estimated to be 20 µm with FeCl$_3$ dosing, instead of 2 µm without. Moreover, without FeCl$_3$ dosing the surface is finely granular, whereas upon dosing it is coarse granular.

Cake porosity calculation
From Figures 2–5 one can calculate the differences in cake porosity with and without FeCl$_3$ dosing. This calculation goes as follows: one compares the observed cake volume (based on cake layer thickness, derived from Figures 2 and 3) with the theoretical cake volume,
based on suspended solids (SS) content in the raw water. Then Eq. (1) is used to calculate the cake porosity:

\[
\text{Cake porosity} = \left[ 1 - \left( \frac{\text{theoretical cake volume}}{\text{practical cake volume}} \right) \right] \times 100 \%
\] (1)

Firstly the theoretical cake volume is determined. It is calculated using the mass of SS put on top of the membrane. This is calculated by multiplying the SS content of the raw water with the flux rate, the membrane surface, and the filtration time. By dividing this obtained SS-mass by its density, one obtains the volume of SS, or the theoretical cake volume. The density of the SS was supposed to be 1 g/cm³.

So theoretical cake volume without FeCl₃ dosing is equal to 12.5 mg/l × 100 l/h/m² × 0.00686 m² × 1 h = 0.00858 g / 1 g/cm³ or 0.00858 cm³.

For cakes formed upon FeCl₃ dosing, the amount of Fe also has to be taken into account. The mass of Fe on the membrane after 1 hour of filtration can be calculated by multiplying the Fe dose (0.7 mg/l) with the flux, the membrane surface, the filtration time:

Theoretical Fe mass = 0.7 mg/l × 100 l/h/m² × 0.00686 m² × 1 h = 0.48 mg Fe

Upon Fe-dosing the following stoichiometric reaction occurs:

\[ \text{Fe}^{3+} + 3 \text{OH}^- \rightarrow \text{Fe(OH)}_3 \]

Since the molecular weight ratio of Fe to Fe(OH)₃ equals approximately 1.9 (more exactly 106.8/56), one mg of Fe equals 1.9 mg of extra suspended solids. The so-formed amount (mass) of Fe(OH)₃ on the membrane equals 0.92 mg.

The volume of Fe(OH)₃ on the membrane after 1 hour filtration is the mass Fe(OH)₃ divided by the density of Fe(OH)₃ (supposed to be rather around 1 g/cm³). This volume is equal to 0.92 mg/1 g/cm³ or 0.00092 cm³. So, the total theoretical cake volume upon FeCl₃ dosing is equal to the sum of the theoretical cake volume of the SS originating from the raw water, with the theoretical cake volume of the formed Fe-hydroxide. This sum equals 0.00949 cm³.

Secondly, the observed (real) cake volume is determined. For the experiment with FeCl₃ dosing it can be derived from Figures 4 and 5, by multiplying the observed cake thickness with the membrane surface, or 0.002 cm × 68.6 cm². This is equal to 0.13723 cm³. The real cake volume for the experiment without FeCl₃ dosing can be derived from pictures 2 and 3. This equals 0.01372 cm³.

The final results of the cake porosity calculations are as follows:

- without coagulant dosing the cake porosity equals 37%
• with FeCl₃ dosing it equals 93%!!

So, it is clear that the use of a coagulant (FeCl₃), even at low dosage, leads to filtration cakes with much more pronounced porosities.

In order to study the indirect effects of in-line coagulation, pilot filtration experiments were done. From studying the stability of the starting TMP in each filtration cycle upon semi-dead-end operation and use of FeCl₃, it was found that it remained very stable over time.

But once the dosing was stopped the TMP was rising very steeply (see Figure 6) under stressing circumstances, such as:
• high flux rates
• high water recovery rates
• using membranes made from polymers with high adsorption properties

From this it was concluded that cake layers formed upon FeCl₃ dosing were less prone to adhere to the membrane surface.

**Search towards the indirect effects of in-line coagulation (dead-end filtration experiments)**

To search for the different indirect effect of in-line coagulation, both short-term and long-term pilot dead-end filtration experiments were performed. The effect of in-line dosing of coagulant was assessed, by looking at the TMP versus time. Different UF pilot membrane modules were tested extensively (Norit/Stork Friesland/Hydranautics/Koch). Two of them were PES/PVP blend membranes, whereas the others (Koch) were PSf and PVDF/PVP (Stork Friesland) membranes. The pore sizes were around 150 kD, and 20 nm for the Stork Friesland membrane. All membranes had an internal diameter of 0.7 to 0.8 mm, except for the Stork Friesland membrane which was 5.2 mm. The clean waterflux of the used membranes was in between 370 and 1,500 l/m²hbar.

For performing these semi-dead-end experiments a filtration pilot, mounted in a 20-foot container, was used. The coagulant is dosed with a dosing pump at the entry of the feed pump. In this way a rapid mixing occurs simultaneously. Different flow-, pressure- and temperature transmitters are foreseen to enable the measurement of permeate flow, retentate flow, feed turbidity, TMP and temperature. The special feature of the unit is the unique MEFIAS® real-time data-acquisition and the MeFiAS® II steering-software for automated operation, developed by Vito. The unit enables carrying-out easily (in an automated manner) the filtration experiments, and facilitates reporting of the results.

**Location of the experiments and water types**

The experiments were performed at three locations (all surface water types), from December 1998 until September 2000. An overview of the different locations and water types is given in Table 1.

From Table 1 we can conclude that waters with quite different and wide varying

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**Figure 6 Effect of stopping FeCl₃ dosing on the TMP versus time**
compositions were investigated; from quite clear to very turbid, and from quite low DOC to high DOC, both waters from reservoir, canal and river.

**Results of the search for the different indirect effects of in-line coagulation**

The observations made were in good agreement with the found higher cake porosity, determined during the earlier filtration cake study.

The different indirect effects of in-line coagulation can be summarised as follows:

- Lower TMP-increase in the filtration cycles is obtained (band-width of only 0.03 bar (see Figure 8) instead of 0.06 bar (see Figure 7), probably due to depth filtration mechanism instead of surface filtration mechanism.
- Much better TMP-stability over longer time due to the higher dirt holding capacity of the formed fluffy cakes and also partly due to lower cake-adherence. TMP increase over 24 h interval with coagulant of only 0.01 bar/24 hours, instead of 0.1 bar without coagulant (see also Figures 7 and 8).
- Another indirect effect of in-line coagulation, in agreement with the lower proneness of adherence of cake, is the disappearance of most of the membrane polymer related properties, to a large extent. Instead of “only one single suitable membrane type for one application”, “multiple membrane types suitable”. In addition, the lower proneness of adherence of cake was further expressed by the fact dosing was not necessary during the whole filtration cycle. Thus, it was found that dosing of coagulant was only necessary during the first 10 to 15 minutes (first half to first third) of the filtration cycle. This observation is in good agreement with EPCE coating method with e.g. Fe(OH)$_3$, introduced by Galjaard *et al.* (2001).

As a result of these indirect effects, other features arise. They can be summarised as follows (similar observations were done with coagulants other than FeCl$_3$):

- Possibility to further improve filtration effectiveness: increase of water recovery; e.g. from 90% to up to 98%, and possibility to increase of flux rate to up to 200 lmh in certain cases.
- Possibility to postpone cleaning action; e.g. from once per week to up to once per several weeks (up to 8). As a consequence less chemicals are needed.
- Possibility to lower the cleaning aggressiveness (use of other cleaning chemicals); e.g. use of sulphuric or nitric acid, instead of sodium hypochlorite, with another indirect effect of extending the membrane life.

**Table 1  Location of experiments and water types**

<table>
<thead>
<tr>
<th>Water type/location</th>
<th>Water company</th>
<th>Source</th>
<th>Major contaminants</th>
<th>DOC (mg/l)</th>
<th>Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kluizen</td>
<td>VMW</td>
<td>Canal (via reservoir)</td>
<td>Low MW components</td>
<td>10</td>
<td>0.2 – 2</td>
</tr>
<tr>
<td>Grobbendonk</td>
<td>Pidpa</td>
<td>Canal (direct intake)</td>
<td>SS, clay, bacteria, (algae)</td>
<td>3</td>
<td>20 – 80</td>
</tr>
<tr>
<td>Korbeek-Dijle</td>
<td>VMW</td>
<td>River (direct intake)</td>
<td>SS, clay, bacteria</td>
<td>4</td>
<td>5 – +100</td>
</tr>
</tbody>
</table>

**Figures 7 and 8** Filtration respectively without (7, left) and with (8, right) FeCl$_3$ dosing
Coagulant dosing also helps facing the influence of seasonal water-quality variations.

Coagulant dosing enables in certain cases the treatment of surface water with high DOC, which normally fouls to great extent the internal structure of an UF membrane.

**Conclusions**

The constant high water quality of UF, which is independent from the operational mode, membrane type or raw water composition, on the one hand, combined with the strongly improved operational mode, on the other hand, makes in-line coagulation UF technology the future replacement of classical water pre-treatment techniques.

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**References**


