Techneau, D5.3.5B
February 2008

Nanofiltration for removal of humic substances

Survey on operational strategies

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TECHNEAU is an Integrated Project Funded by the European Commission under the Sixth Framework Programme, Sustainable Development, Global Change and Ecosystems Thematic Priority Area (contract number 018320).

Colophon

Title
Nanofiltration for removal of humic substances
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Deliverable number
D 5.3.5 B

This report is:
PU = Public

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1 Introduction

Nanofiltration (NF) for the removal of humic substances/natural organic matter (NOM) from water has been used for about 20 years in Norway.

In 2006, 98 plants serving more than 50 people were using this process, and approximately 120 000 people were supplied from waterworks using nanofiltration. The largest of these plants was serving almost 9000 people. Similar plants are in operation in Scotland and Ireland.

In 2006-2007, a survey was performed on the operating experiences of the Norwegian water treatment plants using nanofiltration for the removal of humic substances, and this report is based on the results from that survey.

2 Operational strategies

2.1 Flow sheet

A typical process design of a Norwegian water treatment plants based on nanofiltration (NF) for the removal of NOM/humic and fulvic acids is shown in Figure 1. This process design is the standard for the plants included in this study, even though the pre-treatment and post-treatment may vary.

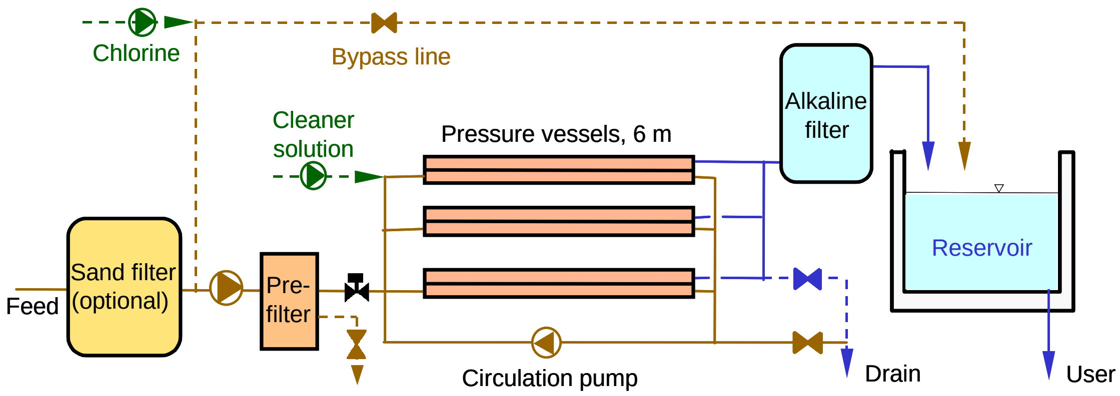

Figure 1. Typical layout of a nanofiltration plant for NOM removal (Thorsen, 1999)

2.2 Pre-treatment

The most common pre-treatment is filtration through a pressure filter with automatic backwashg, reported by 67 % of the plants in 2006. The pore opening in the filters is usually 50 µm, but occasionally filters with pore openings of 100 µm are used. 4 % of the plants used rapid sand filters, and one plant had hardness removal as a pre-treatment. Several plants did not report the type of pre-treatment, but we may assume that the majority of these had pressure filter as pre-treatment.

Some of the nanofiltration plants are evaluating an extension of the pre-treatment due to fouling problems, and in the future more variations in pre-treatment may be assumed.

2.3 Post-treatment

The post-treatment may be disinfection and/or pH adjustment (i.e. corrosion control). A few years ago the common design was to use nanofiltration as the only hygienic barrier, but during the last ten years UV disinfection has been added to existing plants as well as new plants. Approximately half of the Norwegian NF plants had UV-disinfection as post-treatment in 2006. Most of the plants had chlorination equipment installed, but only as a back-up.

Because Norwegian surface waters are normally soft, with low alkalinity and a rather low pH, usually below 7, there is a need for a corrosion control, including pH adjustment. Close to 60 % of the plants used various treatment processes for corrosion control/pH adjustment in 2006, including alkaline filters (27 % of all plants), addition of sodium silicate (17 %), addition of calcium carbonate slurry (10 %), and a few plants adding sodium hydroxide or sodium carbonate.

2.4 Design and operational conditions

The nanofiltration plants for removal of humic substances use spiral wound membranes. The membrane material is usually cellulose acetate, but other materials like polyamide are occasionally used. The nanofiltration plants usually use membranes with nominal pore size ranging from 1-5 nm, and the most common pore size is 1.5-2 nm. The membrane modules are usually approximately 1.5 m long, with 2-4 modules in each pressure tube. The design of the larger plants is based on several tubes in parallel. The module diameter is typical 8 ".

The design flux on the membranes is typical 15-25 $l/m^2 \cdot h$. The recommended cross flow is 5-15 m^3/h for an 8" tube to minimise fouling. The raw water side of the membranes are cleaned daily with a diluted chemical solution and more thoroughly once each year or more frequent when necessary. The cleaning usually includes chlorination. The treated water side of the membranes are usually neither cleaned nor disinfected.

3 Operational experiencies

3.1 Methodology

The survey was based on the following information:

- Statistical information from the authorities on treatment plants with nanofiltration per 2006, including all 98 waterworks supplying more than 50 people
- Raw and treated water quality from the period 2001-2005
- Response from the waterworks on a questionnaire. 37 of 98 waterworks responded.
- Supplementary sampling and water analysis before and after the membrane modules
- Supplementary questionnaire regarding operational problems at 11 waterworks

3.2 Treated water quality

The results presented in this chapter are based on statistical information from the authorities, included raw and treated water quality from the period 2001-2005.

The treated water turbidity is shown in Table 1.

Table 1. Treated water turbidity. The results are given as % of the plants with a yearly average turbidity within the given ranges.

Turbidity range	% of the plants with yearly average turbidity within the range				
	2001	2002	2003	2004	2005
≤ 0,1 FNU	65	50	48	60	46
0.1-0.4 FNU	33	45	46	32	44
>0.4 FNU	2	5	6	8	10

More than 50 % of the plants report average turbidity ≤ 0.1 FNU, and more than 90 % of the plants report average turbidity < 0.4 FNU. Because the nanofiltration plants are expected to remove **all** particles, one may ask for the origin for the turbidities > 0.1 FNU that are reported. Microbiological growth in the treated water, some water bypassing the membrane plant and leakages through the membranes may all be possible explanations.

The nanofiltration plants are built for removal of colour caused by NOM/humic substances, and the colour removal will therefore be a good indicator for the general performance of the process. In Figure 2 the colour in the treated water is shown as a function of the raw water colour.

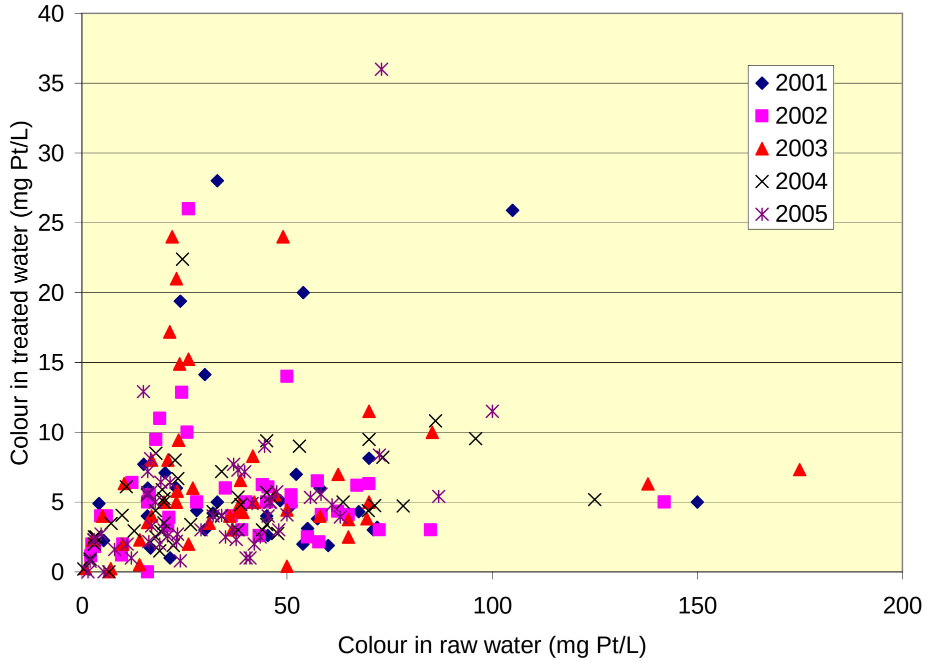

Figure 2. Yearly average colour in treated water as a function of the raw water colour

The treated water colour is mostly below 10 mg Pt/L, but occasionally the colour is much higher. There is no obvious relation between the raw water colour and the reported high treated water colour. This indicates that other factors than the raw water colour is the reasons for this malfunction of the nanofiltration plant. The figure also illustrates that the nanofiltration process may produce satisfactory permeate even with very high raw water colour levels.

When looking into all the single analyses, each year more than 50 % of the plants have experienced colour > 5 mg Pt/L and more than 30 % of the plants have experienced colour > 10 mg Pt/L.

Table 2 summarises the treated water microbiological quality after nano filtration, and for approximately half of the plants also UV disinfection.

Table 2. Microbiological quality in NF-treated water. The results are given as % of the plants that did not meet the required quality for one or more samples during one year. (Please do mind that half of the plants have UV disinfection added to the nanofiltration plant, and sampling was performed after all treatment processes)

Year	% of the plants for which one or more samples in the period 2001-2005 had plate count > 100/mL or where indicator parameters were positive in at least one sample				
	Plate count > 100/mL	Total coliforms	*E. coli*	Enterococci	*Clostridium perfringens*
2005	38	30	6	0	0
2004	29	40	12	2	2
2003	30	20	12	0	0
2002	20	16	6	0	0
2001	25	9	3	0	0

The apparent increase in total coliforms from 2001 to 2004 is partly due to changes in water analysis procedures.

E. coli was detected in treated water once or more at 31 % of the waterworks during these five years. None of the waterworks where *E. coli* was detected in treated water in 2005 had UV disinfection, implying that among the treatment plants without UV *E. coli* was detected in one or more samples at 12 % of the plants this year.

The percentage of the plants with at least one sample with plate counts > 100/mL seemed independent of whether the plants had UV disinfection or not, and no relation between raw water and treated water plate counts could be established. This indicates that the plate counts originate from microbiological growth in the treated water.

Table 3 shows the possible correlation between permeate water quality and selected membrane properties, operational strategies and experiences.

Table 3. Correlation between permeate water quality and selected membrane properties, operational strategies and experiences

	Colour in permeate	Plate count in permeate
Molecular weight cut-off	Yes	Yes
Age of membranes	No	No
Discontinuous production	-	Yes
Failure in the hygienic barrier	No	Yes
Colour in permeate	-	Yes

The higher the molecular weight cut-off for the membrane, the higher was the measured permeate colour, which was no surprise. More surprisingly was the fact that the higher the molecular weight cut-off and the higher the colour level was in the permeate, the higher was also the plate count in the permeate. Possible reasons for high plate count numbers in the permeate will be discussed below.

A discontinuous water production, with stagnant water at the treated water side of the membranes at least parts of the night, increased the plate count in the permeate.

The plants with a high plate count in the permeate were also among the plants with a high degree of failure in the hygienic barrier.

3.3 Operational challenges

The results presented in this chapter are based on the information given from the waterworks in the questionnaires.

The majority of the waterworks declared that they were generally satisfied with the nanofiltration plant. Those who were not satisfied had experienced severe problems with the plant, and some of these problems will be discussed below.

46 % of the plants had experienced operational problems due to the prefilter, and most of these plants had replaced their filter with another type of filter and/or a filter from another producer. The operational problems were fouling/scaling with frequent flushing as a result, or insufficient hydraulic capacity.

40 % of the plants had experienced fouling. The remaining 60 % did not know whether they had fouling, but one may assume that fouling did not cause major operational difficulties at these plants. To what extent the experienced fouling had caused an impact on performance varied considerably, but several plants had experienced major decreases in water production rates/treatment capacity. Partly organic and partly inorganic compounds were reported as the most likely cause of the fouling, while only one plant had experienced that biological growth on the raw water side of the mem-

branes was the cause. Some plants had solved their problem by installing more membrane modules in parallel with the existing plants, one plant had experienced that the fouling problem could be solved by exchanging the pre-filter with a filter from another supplier, while other plants still do not have a satisfactory solution. An improper pre-treatment is the most common cause of fouling, often combined with a too optimistic design load. The designed hydraulic load is typically between 15 and 25 $L/m^2 \cdot d$, while experience indicates that the load should be below 20 $L/m^2 \cdot d$. There was no correlation between fouling and the raw water colour, turbidity or pH levels, even though organic or inorganic particles most certainly caused the fouling.

The service time of the membranes was typically 6-10 years, but varied considerably. The rather high colour in the permeate at the two plants with service times more than ten years indicate that these membranes should have been renewed.

All the waterworks that use nanofiltration assumed originally that this treatment process would also be a hygienic barrier towards pathogens. 27 % of the plants reported in the questionnaires one or several failures in this barrier during the period 2001-2006, a lower number than indicated by the results presented in Chapter 3.2. The failures were not discovered before coliforms were proven in the treated water, showing the lack of reliable indicators for the performance of this barrier. Neither colour nor turbidity in the treated water gave any early warning of the failure, maybe partly because the failure is limited to one membrane or a few membranes and the fact that the samples are normally taken from the plant outlet and not from each membrane module.

There have been several different reasons for the failure in the hygienic barrier. Leakages through the contactors between the membranes because of defect O-rings, leakages through the membranes because of breakage as well as raw water accidentally by-passing the membranes modules were proven reasons, but often the reason was unknown. Some plants indicate that failure in the pre-filter was the indirect reason, since this caused fouling and high pressure loss and finally breakages. Inappropriate plant design, like intermittent pre-filters that caused frequent variations in the inlet pressure, did also cause breakages.

Several nanofiltration plants had experienced microbiological growth in the treated water, causing higher plate count numbers than recommended. Approximately 30 % of the plants had experienced a high plate count, > 100/mL, once or several times, often with a low plate count in the raw water, while the micro-organisms are expected to be removed in the plant. One possible explanation is that there may be a considerable biofilm formation on the treated water side of the membranes in these plants. Hem and Charnock (1999) found that the biofilm formation potential, determined as assimilable organic carbon (AOC), was not reduced during nanofiltration, while Hem and Efraimsen (2001) found that AOC was mainly related to NOM with a molecular weight below 1000. The potential for microbiological growth in the treated water can therefore be explained. The occurrence of high plate count numbers were in particular frequent at plants with no water production during night-time, and with stagnant water at relatively high temperature (up to 20 °C) at the treated water side of the membranes. The phosphate content in the cleaning solution had no apparent influence on this microbiological growth.

Table 4 shows the AOC results from one sampling and analysis in the autumn 2007 at two plants, as well as the summarized plate count data for the period 2001-2005.

Table 4. Plate count numbers and AOC data from two NF plants. The permeate samples were taken prior to disinfection

Parameter	Plant 1		Plant 2	
	Raw water	Permeate	Raw water	Permeate
AOC (µg/L) autumn 2007	45	23	48	22
Plate count (/mL) autumn 2007	890	100	-	-
Average plate count (/mL) 2002-2005	205	65	106	121
Max. plate count (/mL) 2002-2005	1400	530	400	2400

As shown by the results in Table 4, AOC levels were considerably reduced in the two plants, while the plate count was slightly reduced at one of the plants and increased at the other plant. The results indicate a considerable microbiological growth that both removes some AOC and increases the plate count.

4 Actions to improve operational performance

4.1 Keep records

When an operational problem occurs, there will of course be a need for immediate corrective actions. Then it is important that a correct plant description, including design data, is available. When for instance fouling causes reduced hydraulic capacity, a proper record will help to recognize the problem and to identify the cause. Some important operational data that should be present in the record are:

- Water production/permeate (m^3/h)
- Operational pressure at the pressure tube inlet (bar)
- Operational pressure at the pressure tube outlet (bar)
- Cross-flow circulation rate (m^3/h)
- Concentrate production rate (m^3/h)
- Water temperature (°C)
- All relevant events

4.2 Adequate pre-treatment

The pre-treatment is more or less standardised to 50 µm filters with automatic backwashing. This standardisation is proven to be unsatisfactory, since some plants have difficulties with their pre-treatment even with filters that show good performance at several other plants.

There should be a thorough study of the raw water quality as a basis for design, and this should in particular give information on particles with a fouling potential for the membranes, as will be discussed below. The design basis should of course also be sufficient to give a proper design of the pre-treatment itself, whether this is a prefilter or a more extensive treatment.

4.3 Fouling control and actions to avoid fouling

“True” fouling is mainly caused by particles with diameter 0.1-5 µm. In addition, larger particles can accumulate in the spacer grid and microbiological growth can cause bio-fouling.

Accumulation in the spacer grid can usually be avoided with a proper 50 µm prefilter, but occasionally a filter that can remove parts of the particles smaller than 50 µm may be necessary.

Biofouling may be avoided by a choice of a cleaning solution that contains a biocide.

In order to avoid “true” fouling, several actions may be relevant:

- The design flux should not exceed 0.20 $\mathrm{l/m^2 \cdot h}$. If a considerable fouling potential does exist, the design flux should be lowered towards 0.15 $\mathrm{l/m^2 \cdot h}$.
- The rate of crossflow should be 5-11 $\mathrm{m^3/h}$ for 8″ spiral membranes. With a water production rate of 3.5 $\mathrm{m^3/h}$, the circulation flow rate should be at least 8.5 $\mathrm{m^3/h}$ in order to maintain the necessary crossflow for all membranes in a 6 m pressure tube.
- Reduced permeate recovery gives an increased concentrate flow rate and a reduced particle concentration in the circulation flow. Application of this fouling control strategy is however dependent on a sufficient capacity of the raw water source.
- The membrane material may influence the fouling. While regenerated cellulose and polyamide suffered little from adsorptive fouling, cellulose acetate showed moderate and polysulphone severe adsorptive fouling (Thorsen, 1999).

Two parameters that can describe the long-term fouling are the developments in the permeability and the crossflow pressure loss. For an 8″ spiral membrane with a 6 $\mathrm{m^3/h}$ crossflow rate these parameters can be described as follows (Thorsen, 2007):

$$Permeability = \frac{(inlet\ \ flux + outlet\ \ flux)}{2} \cdot \frac{[1 + 0{,}025 \cdot (6 - temperature)]}{average\ \ pressure\ loss}$$

where the average pressure loss is the pressure at the raw water side minus the pressure at the treated water side of the membrane

or

$$Permeability = (average\ \ flux) \cdot \frac{[1 + 0{,}025 \cdot (6 - temperature)]}{average\ \ pressure\ loss}$$

$$Crossflow\ \ pressure\ loss = (inlet\ tube\ \ pressure - outlet\ tube\ \ pressure) \cdot \left(\frac{6 \cdot 2}{inlet\ crossflow + outlet\ crossflow} \right)^{1{,}8}$$

The permeability is an indicator for “true” fouling, while the crossflow pressure loss is an indicator for fouling/accumulation in the spacer grid. If these two parameters are frequently recorded, one may get an early warning of the fouling.

4.4 Actions to reduce biofilm formation on the membranes

The huge area on the treated water side of the membranes makes biofilm formation a most likely possibility. However, some of the operational strategies may influence the microbiological growth:

- At plants with almost no water production during night time, the water on the treated water side of the membranes is stagnant, and the water temperature increases from typical raw water temperatures of 4-10 °up towards room temperature and there is no flow through the membranes. This may increase microbiological growth in the water and on the membranes. A change to continuous water production should then reduce the biofilm formation.
- None of the plants had routines for cleaning the treated water side of the membranes. When the biofilm is established, no present operational action will remove the film. By establishing a routine for such cleaning, the biofilm formation and the depreciated water quality following this formation, may be reduced. However, both the routine and the cleaning agent should be chosen in collaboration with the membrane supplier, in order to reduce the risk for membrane damage.

4.5 Actions to prevent and detect failure in the hygienic barrier

Actions to avoid unsatisfactory treated water quality caused by failure in NF as a hygienic barrier can be divided into two different categories:

- Methods to detect failure
- Actions to prevent failure

Usually, failures were not detected before coliforms, and sometimes even *E.coli*, were detected in treated water. The failure itself may have been present for several months, and even years, before it was detected. This situation is due to the lack of reliable indicators for nanofiltration as a hygienic barrier. Ongoing projects deal with the possibility of identifying indicators or methodology that can be used to prove that the barrier is valid and well-functioning.

The reasons for failure in the hygienic barrier include a variety of design and operational issues. Some of these issues, like the importance of a proper pre-treatment, are discussed above. An issue that should be addressed in the future is the service time of the membranes as well as the contactors, O-ring etc. Even if the colour removal indicates that the service time may be prolonged, the requirement for the nanofiltration as a hygienic barrier may give reason to more frequent exchanges of membranes and O-rings.

5 Conclusions

The plant design and operational strategies are to a large extent standardised for all the Norwegian nanofiltration plants. However, both due to operational experiences and the need to increase the barrier efficiency in the water treatment plant, several waterworks have modified the treatment process. The most frequent modifications are renewed prefilters and addition of post-disinfection with UV.

The treated water quality is satisfactory at the majority of the treatment plants, but during the last years approximately 30 % of the plants have at least once a year measured colour > 10 mg Pt/l. 30 % have detected total coliforms in the treated water at least once a year and 31 % have detected *E.coli* in the treated water once or more in the period 2001-2005.

The reported operational problems experienced at the nanofiltration plants are:

- Fouling/scaling on the prefilter, or insufficient hydraulic prefilter capacity (46 % of the plants)
- Membrane fouling (40 % of the plants)
- Failure in the hygienic barrier (27 % of the plants)
- High plate count numbers in the permeate (30 % of the plants)

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