

Direct capillary nanofiltration for ground water and surface water treatment

J.Q.J.C. Verberk*†, J. Post**, W.G.J. van der Meer*** and J.C. van Dijk*

* Department of Civil Engineering and Geosciences, Delft University of Technology, PO Box 5048, 2600 GA Delft, The Netherlands (E-mail: j.q.j.c.verberk@citg.tudelft.nl)

** DHV Water, PO BOX 484, 3800 AL Amersfoort, the Netherlands (E-mail: jan.post@dhv.nl)

*** Nuon Water, PO BOX 400, 8901 BE Leeuwarden, the Netherlands (E-mail: walter.van.der.meer@nuon.com)

† corresponding author

Abstract Capillary nanofiltration is a new concept in membrane filtration. This technique combines the advantages of the good water quality obtained from nanofiltration membranes with the easy hydraulic cleaning of capillary membranes. Direct capillary nanofiltration can be used to treat ground water or surface water without pre-treatment. At the Delft University of Technology several MSc-thesis projects have been carried out on this subject. This paper will describe some results of these studies. A model based on a mass balance to predict the flux of a capillary nanofiltration installation treating groundwater is proposed. In this model the only resistance taken into account is the concentration polarisation. Also a model to predict the flux when treating surface water has been developed. This model takes into account the resistance due to cake filtration.

Keywords Capillary; concentration polarisation; ground water; modelling; nanofiltration; surface water

Introduction

Membrane technology is used widely for the production of drinking or process water. The quality of the desired product determines which membrane type is used. Nanofiltration membranes remove bacteria, viruses, organic substances, hardness and organic micro-pollutants and are therefore often applied.

In nanofiltration installations spiral wound membrane modules are most common. The specific membrane area (installed membrane area per module) of spiral wound membranes is large, resulting in low investment costs. However, a disadvantage of spiral wound modules is the extensive pre-treatment needed. Because of the small height of the feed spacers spiral wound membranes will foul rapidly. Unlike micro- and ultrafiltration membranes spiral wound membranes can't be cleaned hydraulically. To prevent fouling of the spiral wound nanofiltration membranes an extensive pre-treatment, consisting of conventional drinking water processes or ultrafiltration, is necessary, usually in combination with dosing of chemicals (anti-scalants, acids) to prevent fouling and clean the membrane surface.

Capillary membranes are used in micro- and ultrafiltration applications. Due to the larger pore size of ultrafiltration membranes, the water quality is less than the water quality obtained with nanofiltration and reverse osmosis. Micro- and ultrafiltration are mainly used to remove suspended matter from the water. Micro- and ultrafiltration membranes can be cleaned hydraulically. Several hydraulic cleaning methods can be used, like backflush, forward flush and AirFlush® (combined air and water forward flush).

Capillary nanofiltration combines the advantages of nanofiltration membranes (good water quality) and capillary ultrafiltration membranes (good cleaning possibility). It appears to be possible to treat (surface) water in one single treatment step to high quality

process water. This concept of direct capillary nanofiltration has been developed by X-Flow (formerly Stork Friesland), DHV Water and Nuon.

In the Netherlands several feasibility studies with pilot plants have been performed with this new technique. Effluent from a sewage treatment plant and surface water has been treated (van der Meer *et al.*, 2001).

Process description

The process can be compared to dead-end ultrafiltration. A direct capillary nanofiltration module is placed vertically. During a certain time period water is filtered. During this filtration period only permeate is produced and no concentrate is discharged (Figure 1). The permeate flow is only about 10% of the total flow. After some time the installation is flushed, all the water in the system is removed. Because of this discontinuous discharge of concentrate, the process is sometimes called dead-end capillary nanofiltration. During the filtration phase there is an accumulation of substances (salts, suspended matter) in the installation. As a result of this accumulation problems with scaling, deteriorating permeate quality, decrease in flux due to higher osmotic pressure and fouling could occur. To prevent these problems water is continuously recirculated. After some time the installation is flushed.

Modeling

In traditional spiral wound membrane filtration processes the parameters to control the installation are the Trans Membrane Pressure (TMP) and the flux. Several theoretical models have been developed to describe the process and to optimise the design of membrane filtration modules/installations (van der Meer *et al.*, 1997). With direct capillary nanofiltration additional parameters can be used to optimise the installation. Additional to the TMP and flux also filtration time and cross flow velocity are variables. For a further development of this new technique a better process understanding is necessary. A model, based on a mass balance, has been developed and will be described hereafter.

Like with every membrane filtration process the performance of direct capillary nanofiltration will decrease in time. From the theory of membrane filtration and fouling the following different fouling mechanisms are known (Mulder, 1996):

- pore blocking;
- adsorption;
- gel layer formation/cake filtration;
- concentration polarisation.

When using direct capillary nanofiltration to treat surface water, concentration polarisation and cake filtration will occur simultaneously. It is difficult to model both phenomena at the same time. Therefore we have tried to develop separate models to describe both phenomena.

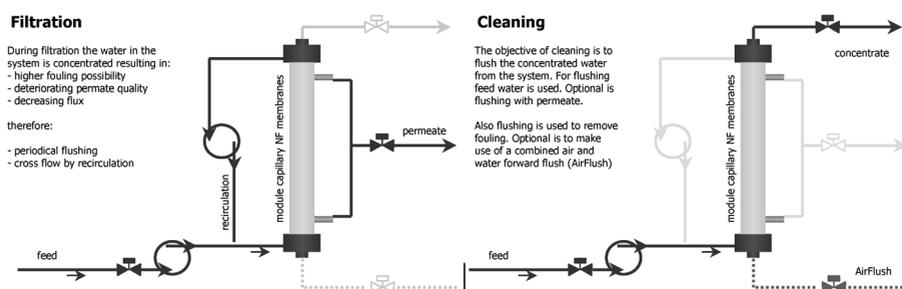


Figure 1 Operation of direct capillary nanofiltration

Direct capillary nanofiltration and concentration polarisation

To take into account the effect of concentration polarisation and osmotic pressure losses, it is necessary to know the concentration of salts in the system. The recovery of a direct capillary nanofiltration system is defined as:

$$\gamma = \frac{V_{perm}}{V_{feed}}$$

- γ = recovery [-]
- V_{perm} = permeate volume [m³]
- V_{feed} = feed volume [m³]

The permeate volume is equal to the permeate flow times the production time. The feed volume is the produced volume together with the volume of water used for cleaning the system. When the system is cleaned, the volume in the system is flushed out of the module. In the most ideal situation (plug flow) the amount of water used for cleaning is equal to the volume of the system. In practice more water will be used to clean the system. The number of times the system is “refreshed” is expressed with the parameter α . The number of times the installation produces its own volume is given by the parameter τ

$$\tau = \frac{Q \cdot t_f}{V_{sys}}$$

With the parameters α and τ the recovery γ can be rewritten as

$$\gamma = \frac{\tau \cdot V_{sys}}{\tau \cdot V_{sys} + \alpha \cdot V_{sys}} = \frac{\tau}{\tau + \alpha}$$

- τ = number of times installation produces its own volume [-]
- α = number of times installation is flushed [-]
- V_{sys} = volume of system [m³]
- Q = production flow [m³/h]
- t_f = filtration time [h].

In Figure 2 a schematic drawing of the capillary nanofiltration system is given. For the system of direct capillary nanofiltration a mass balance can be made (Post, 2000).

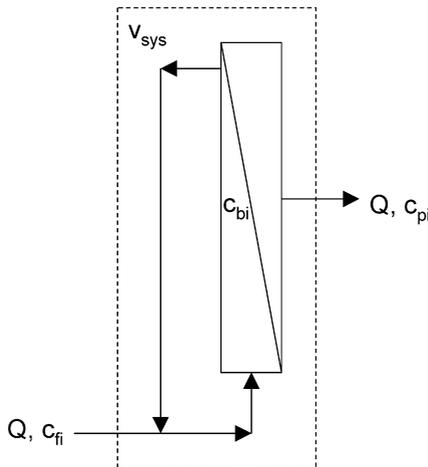


Figure 2 Schematic drawing of CNF installation

$$Q \cdot c_{fi} = Q \cdot c_{pi}(t) + V_{sys} \cdot \frac{dc_{bi}(t)}{dt}$$

- Q = production flow [m³/s]
 c_{fi} = concentration of salt i in feed water [g/m³]
 $c_{pi}(t)$ = concentration of salt i in permeate [g/m³]
 $c_{bi}(t)$ = concentration of salt i in system [g/m³]
 V_{sys} = volume of membrane system [m³].

The concentration of a salt i in the permeate is given by:

$$c_{pi}(t) = (1 - R_{mi}) \cdot \beta_i \cdot c_{bi}(t)$$

- β_i = concentration polarisation salt i [-]
 R_{mi} = retention salt i [-].

The following differential equation is obtained

$$V_{sys} \cdot \frac{dc_{bi}(t)}{dt} + Q \cdot (1 - R_{mi}) \cdot \beta_i \cdot c_{bi}(t) = Q \cdot c_{fi}$$

with as general solution

$$c_{bi}(t) = \frac{c_{fi}}{(1 - R_{mi}) \cdot \beta_i} \cdot \left(c_{bi}(0) - \frac{c_{fi}}{(1 - R_{mi}) \cdot \beta_i} \right) \cdot \exp[-(1 - R_{mi}) \cdot \beta_i \cdot \tau]$$

When the system is cleaned, the boundary condition $c_{bi}(0) = c_{fi}$ is valid, resulting in

$$c_{bi}(t) = \frac{c_{fi}}{(1 - R_{mi}) \cdot \beta_i} \cdot (1 + (1 - R_{mi}) \cdot \beta_i - 1) \cdot \exp[-(1 - R_{mi}) \cdot \beta_i \cdot \tau]$$

$$c_{pi}(t) = c_{fi} \cdot (1 + (1 - R_{mi}) \cdot \beta_i - 1) \cdot \exp[-(1 - R_{mi}) \cdot \beta_i \cdot \tau]$$

The osmotic pressure in the system will also increase in time, because of the increase of the salt concentrations in the system

$$\Delta\pi(t) = \sum_i \Delta\pi_i(t)$$

$$\Delta\pi_i = \frac{R \cdot T \cdot z_i}{M_i} \cdot (c_{mi}(t) - c_{pi}(t)) = \frac{R \cdot T \cdot z_i}{M_i} \cdot \beta_i \cdot R_{mi} \cdot c_{bi}(t)$$

- $\Delta\pi_i(t)$ = osmotic pressure difference of salt i [Pa]
 R = universal gas constant [8.31 J/(K·mol)]
 T = temperature [K]
 M_i = molecular mass of salt i [kg/mol]
 z_i = valence of salt i [-].

When the system is operated at constant permeate flow (constant flux), the feed pressure should increase in the same amount as the increase in osmotic pressure.

$$J_w = K_{mw} \cdot (P(t) - \Delta\pi(t))$$

- K_{mw} = permeability constant [m/(s·bar)]
 $P(t)$ = feed pressure [bar].

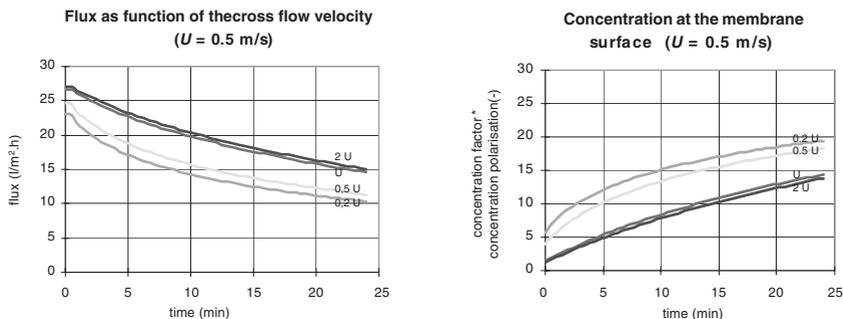


Figure 3 Flux and concentration as function of cross flow velocity and time

The influence of the cross flow velocity becomes clear if we take a closer look at the concentration polarisation factor β_1 .

$$\beta_1 = \frac{c_{mi}}{c_{bi}} = \frac{\exp(J_w / k_i)}{R_{mi} + 1 - R_{mi} \cdot \exp(J_w / k_i)}$$

According to this equation the concentration polarisation factor is influenced by the retention, the flux and the mass transfer coefficient. The retention of membranes is independent of the liquid velocity (Worm *et al.*, 2001), and thus the mass transfer is determined by the hydraulics of the system. Figure 3 shows that a higher flux and retention are found when using higher recirculation velocities. This is caused by the lower polarisation factor. The increase of flux and the higher retention will result in an increase in concentration in the system. However the effect of the lower polarisation factor is bigger than the increase in osmotic pressure.

With the described model it is possible to determine the influence of a change in one of the operational parameters. Also the predicted water quality is in good correspondence with the measured values under laboratory conditions. In practice this model can be used to predict the salt concentrations in the permeate for all kind of applications.

Direct capillary nanofiltration and fouling

The modelling of the resistance caused by fouling is more complicated. Adsorption, pore blocking and cake filtration occur at the same time when treating surface water. With direct capillary nanofiltration the pores of the membrane are very small and we therefore assume that pore blocking will be small.

Suspended matter will be deposited on the membrane surface by the water permeating the membrane. At the same time the recirculation flow will remove deposited material. In this way the cake layer is controlled by the recirculation flow. After some time a hydraulic cleaning is performed. The cake layer will now be removed from the membrane surface, while material adsorbed on the membrane surface will not be removed. A chemical cleaning is necessary to remove this material.

For the different phases as depicted in Figure 4 a model was developed. The filtration phase was described by a model taking into account supply and removal of suspended matter (Nagaoka *et al.*, 1998). The hydraulic cleaning and chemical cleaning were expressed as a percentage removal of the cake layer.

The resistance during a production run consists of 3 different parts (neglecting the osmotic pressure):

- membrane resistance (R_m)
- hydraulic removable resistance (R_{hc})
- chemical removable resistance (R_{cc}).

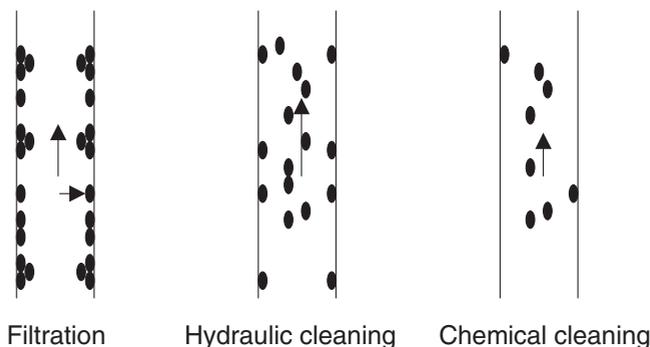


Figure 4 Phases in modelling direct capillary nanofiltration treating surface water

The relation between flux, trans membrane pressure and resistance is now given by

$$\text{TMP} = \frac{1}{1000 \cdot 3600} \cdot J \cdot \eta \cdot (R_m + R_{hc} + R_{cc})$$

- TMP = trans membrane pressure [Pa]
 J = flux [$\text{m}^3/(\text{m}^2 \cdot \text{s})$]
 η = dynamic viscosity [$\text{Pa} \cdot \text{s}$].

The hydraulic removable resistance R_{hc} is given by the relation of Nagaoka (Nagaoka *et al.* 1998)

$$\frac{dR_{hc}}{dt} = \frac{1}{3600} \cdot J \cdot a \cdot \text{NTU}_{\text{sys}} - k \cdot R_{hc}$$

- a = constant [-]
 NTU_{sys} = turbidity in the system [-]
 k = detachment rate of material from the membrane surface [s^{-1}].

$$k = g \cdot (\tau_m - \lambda_m \cdot \text{TMD})$$

- g = constant [$1/(\text{bar} \cdot \text{s})$]
 τ_m = shear stress [Pa]
 λ_m = static friction coefficient [-].

The chemical removable resistance is given by the relation of Tansel (Tansel *et al.*, 2000)

$$\frac{dR_{cc}}{dt} = \omega \cdot R_{cc}$$

- ω = fouling rate chemical removable resistance [s^{-1}].

By numerical integration with Euler's method the given relations can be solved. Different parameters (a , ω , g , λ_m) have to be calibrated before description of the process is possible.

In Figure 5 the total resistance calculated from field tests is compared with the predicted total resistance. It can be seen that the model predicts the total resistance for these runs quite well. However, predicting the resistance over a longer time period in which the module is chemically cleaned is more complex and more effort will have to be given to calibration of the different parameters. Especially attention should be given to a method to characterize the feed water and to the interaction between the particles in the feed water and the nanofiltration membrane.

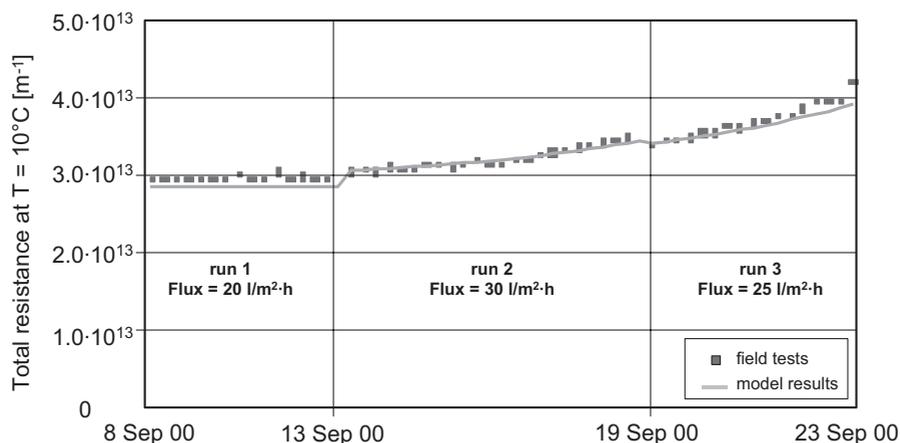


Figure 5 Comparison between resistances from field tests and model at different fluxes

Discussion

To obtain a better understanding of the process of direct capillary nanofiltration, models have been developed. The model describing the concentration polarisation shows encouraging results. The model describing the fouling needs further improvement.

Conclusion

Direct capillary nanofiltration is a new concept in membrane filtration. The system has a number of optimisation parameters (trans membrane pressure, flux, recirculation velocity and filtration time). With capillary nanofiltration it is possible to treat raw water in one step to permeate which can be used as process water. Different pilot studies have shown the possibilities of capillary nanofiltration. Model approaches are formulated for better understanding of the system. The model describing the increasing salt concentration and the concentration polarisation shows encouraging results. The results from the model are in correspondence with results found in pilot installations. Modelling the fouling caused by cake filtration and adsorption when surface water is treated needs further attention.

References

- Meer, van der W.G.J., Schonewille, H. and Efferen, van, B. (2001). Nanofiltration of surface water without pretreatment. *Proceedings of Aachener Tagung*, W14, 1–11.
- Meer, W.G.J. van der and Dijk, J.C. van (1997). Theoretical optimization of spiral-wound and capillary nanofiltration modules. *Desalination*, **113**, 129–146.
- Mulder, M. (1996). *Basis Principles of Membrane Technology*. Dordrecht.
- Nagaoka, H., Yamashita, S. and Miya, A. (1998). Modelling of biofouling by extracellular polymers in a membrane separation activated sludge system. *Water Science and Technology*, **38**(4–5), 497–504.
- Post, J. (2000). *Recovery+, a higher recovery with capillary nanofiltration* (in Dutch), MSc-thesis, Delft University of technology, Delft.
- Tansel, B., Bao, W.Y. and Tansel, I.N. (2000). Characterisation of fouling kinetics in ultrafiltration systems by resistances in series model. *Desalination*, **129**, 7–14.
- Worm, G.I.M., Nederlof, M.M. and Dijk, J.C. van (2001). Liquid velocity-premeate quality relationship for capillary nanofiltration. *Desalination*, **139**, 255–262.