Desalination, 38 (1981) 339—348
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

PREDICTING FLUX DECLINE OF REVERSE OSMOSIS MEMBRANES

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ABSTRACT

A mathematical model predicting flux decline of reverse osmosis membranes due to colloidal fouling has been verified. This mathematical model is based on the theory of cake or gel filtration and the Modified Fouling Index (MFI). Research was conducted using artificial colloidal solutions and a pilot plant equipped with ultrafiltration membranes. Polystyrene latex spheres, having a size of about 0.05-0.08 μm were used as a foulant.

The result of this research was, that the measured and calculated values of flux decline of the ultrafiltration membranes as a function of time agree reasonably well. The difference between the measured and calculated values may be explained by the assumption, that initially blocking filtration occurs instead of cake or gel filtration

INTRODUCTION

An important problem arising in reverse osmosis technology is flux decline of the membranes due to fouling. In many cases flux decline ma be attributed to the presence of colloids in the feed water.

Generally the Silt Density Index is supposed to be a measure of the rate of colloidal fouling to be expected. Experiments with a 7 m^3/h reverse osmosis pilot plant equipped with spiral wound elements and processing pretreated surface water, however, indicated that this view is generally incorrect. The results of calculations using a recently developed mathematical model lead to the same conclusion (1). This model is based on the Modified Fouling Index (MFI), which has especially been developed for measuring the fouling potential of reverse osmosis feed water (2).

Measurements of the MFI-value of pretreated river Rhine water using Nuclepore membrane filters of 0.015-0.8 µm pore size indicated, that this value sharply increases with decreasing pore size. This may be attributed to the presence of small colloids in the water. In table 1 this is illustrated for river Rhine water at Andijk, which is treate by microstraining, chlorination, coagulation, sedimentation and rapid sand filtration.

TABLE 1
MFI-value as a function of pore size of the membrane filter

pore size (m)	MFI (s/l^2)
0.8	4
0.4	60
0.2	200
0.1	1800
0.05	4500
0.015	2000000

Research conducted with the pilot plant described above and calculations using the mathematical model showed, that the colloids rejected by a 0.45 µm membrane filter cannot be responsible for the flux decline observed. From calculations using the mathematical model could be concluded that colloids of a size of 0.05 µm or less are responsible for flux decline of the reverse osmosis membranes.

As the fouling potential of the feed water of the Andijk reverse osmosis pilot plant was subject to considerable fluctuations, the mathematical model could not be verified with sufficient accuracy. This is the reason that research was carried out with artificial colloidal solutions. Preliminary experiments with silica (Ludox HS40, Dupont), polyethyleneglycol, albumine and polystyrene colloidal solutions indicated that the latter is most suitable for this purpose. The experiments were conducted with ultrafiltration instead of reverse osmosis membranes to be certain that the flux decline observed can only be attributed to colloidal fouling and not to the deposition of compounds of low solubility.

MATHEMATICAL MODEL

The Modified Fouling Index is based on the theory of cake or gel filtration. This phenomenon can be described by the following equation:

$$\frac{1}{A} \cdot \frac{dV}{dt} = \frac{1}{\eta} \cdot \frac{\Delta P}{R_f + R_b + R_c} \qquad (1)$$

where:

V = filtrate volume
t = time
η = viscosity
ΔP = pressure drop across the filter
A = membrane area
R_f = resistance of the filter
R_b = resistance due to blocking filtration or concentration polarization
R_c = resistance of the cake or gel

When no compaction of the cake occurs, R_c can be calculated by the following equation:

$$R_c = \frac{I.V}{A} \qquad (2)$$

I is a measure of the fouling potential of the water. Combination of equations (1) and (2), followed by integration at constant ΔP, yields:

$$\frac{t}{V} = \frac{\eta.\ (R_f + R_b)}{A.\Delta P} + \frac{\eta.I.V.}{2\Delta P.A^2} \qquad (3)$$

The Modified Fouling Index is defined as:

$$MFI = \frac{\eta.I}{2\Delta P.A^2} \qquad (4)$$

where:

ΔP = 210 kPa
η = $\eta(20°C) = 1.0050.10^{-3}$ Ns/m^2
A = $\frac{\pi}{4}.(4.2.10^{-2})^2$ m^2, being the geometric membrane area of a membran filter

According to Belfort (3) the mechanism of the deposition of colloids on a membrane is mainly cake or gel filtration. Filtration through a reverse osmosis membrane on which deposition of colloids occurs, can be described by the following equation:

$$F = \frac{1}{A_r} \cdot \frac{dV_r}{dt_r} = \frac{\Delta P_r}{\eta r\ (R_{rf} + R_{rb} + R_{rc})} \qquad (5)$$

where:

F = membrane flux

r = subscript indicating that the parameter refers to a reverse osmosis membrane

ΔP = pressure drop across the membrane minus the difference in osmotic pressure between feed water and product water

The resistance of the filter cake on the reverse osmosis membrane can be calculated from the equation:

$$R_{rc} = \frac{I_r\ V_r}{A_r} \qquad (6)$$

When R_{rb} is assumed to be negligible, combination of the equations (1), (2), (3), (4), (5) and (6) yields after integration at constant ΔP:

$$t_r = \frac{\eta 20°C . \Delta P_r}{2\, \eta_r . F_o^2 . \alpha . \beta .\ (MFI) A^2 . \Delta P} \cdot \frac{\Delta f(2-\Delta f)}{2(1-\Delta f)^2} \qquad (7)$$

where:

tr = the time in which a certain prefixed flux decline is reached

Fo = membrane flux at t = o

$\Delta f = \frac{F_o - F}{F_o}$

α = ratio of the characteristics of the cake or gel on the membrane filter and on the reverse osmosis or ultrafiltration membrane

β = fraction of colloids deposited, which are present in the water passing the reverse osmosis or ultrafiltration membrane

After integration at constant flux F is found:

$$t_r = \frac{\eta\ 20°C\ \ (\Delta P_r - \Delta P_{or})}{2\eta_r . F^2 . \alpha . \beta . (MFI) A^2 .\ \Delta P} \qquad (8)$$

where:

tr = the time in which a certain prefixed increase in pressure is reached
P_{or} = net pressure drop at t = o

EXPERIMENTAL

MFI-measurement

The MFI-value was measured with the apparatus described in ref.(2). For the measurements mainly Nuclepore membrane filters were applied. The filtrate volume as a function of time was measured with a Brooks Micro Oval II flowmeter, model 4150, equipped with a computing totalizer 4250-BB1B4E0 and with a modified device to measure low flux values.

Ultrafiltration pilot plant

The ultrafiltration installation consisted of a pump, measuring and control equipment and four identical tubular ultrafiltration membranes arranged in series. The brine of the installation was not recirculated. The ultrafiltration membranes, manufactured by Wafilin B.V., were made of polysulfone and had a diameter of 1.7 cm and a length of 49 cm.

Foulant

Experiments were carried out with silica sol (Ludox HS40), polyethylene glycols, albumine and polystyrene latex, the latter being the most suitable for further experiments.

Silica sol appeared to be insufficiently stable, which may be caused by dissolution. Polyethylene glycols and albumine colloids were found to be less suitable, because they were not completely rejected by the 0.015 µm and the 0.05 µm Nuclepore membrane filters. Polystyrene latex (PSL), prepared by emulsion polymerization according to Woods (4) did not show the disadvantages mentioned, so that this colloidal solution was used for further experimentation.

Particle size of the PSL spheres was estimated by MFI-measurements with 0.05 µm membrane filters of a solution containing 175 mg/l PSL.

From the MFI-value measured and the MFI-value calculated by the Carman-Kozenzy equation for an assumed value of porosity of the gel layer could be concluded that the PSL spheres have dimensions within the range of 0.05-0.08 µm. The result of the determination of particle size with an electron microscope appeared to be insufficiently accurate, which was probably due to the presence of detergent.

Experimental procedure

Before conducting fouling experiments with the ultrafiltration membranes it was verified whether cake or gel filtration occurs when a PSL-solution is filtered through a 0.05 µm membrane filter. Solutions of different PSL-concentrations were prepared in tap water, that was demineralized and subsequenty filtrated through ultrafiltration membranes. The MFI-value of this water was about 3000 s/l^2. The results are illustrated in figure 1. The linear relationship between $\frac{t}{V}$ and V for different PSL-concentrations indicates, that really cake or gel filtration occurs.

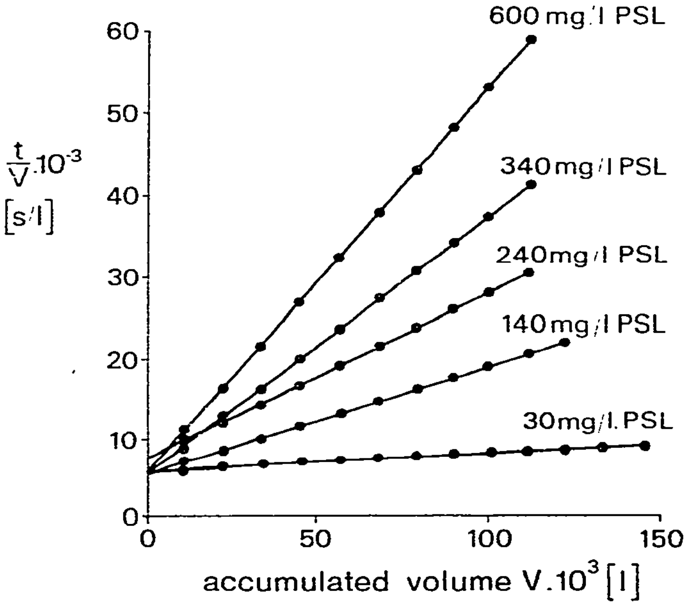

Fig. 1. Filtration curves of PSL-solutions with 0.05 µm membrane filters at 210 kPa.

Figure 2 shows the MFI-value as a function of the PSL-concentration. The figure illustrates the linear relationship expected for PSL.

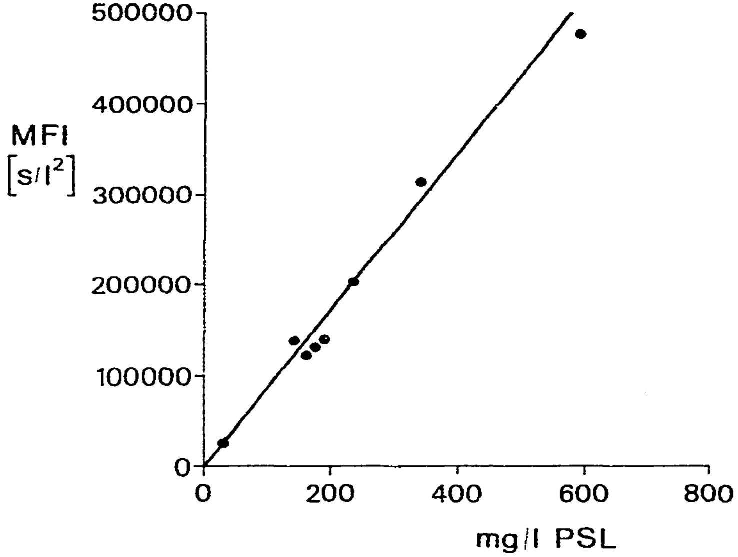

Fig. 2. Relation between MFI (0.05 µm) and PSL-concentration.

The PSL-concentrations were measured with the Beckman Total Organic Carbon Analyzer. The values were corrected for the presence of detergent.

Subsequently research was conducted with the ultrafiltration installation. After measuring flux decline due to compaction and fouling by colloids present in the demineralized, ultrafiltrated feed water, the installation was fed with a PSL-solution. In order to reduce the experimental problems, the experiments were planned such that a run could be terminated within one or two days. The PSL-concentration was chosen in accordance with this. The linear velocity along the membranes was adjusted to <0.04 m/s in order to attain a constant deposition of 100 % on the membrane (β=1) during the run. The percentage of deposition of the colloids during the experiments was calculated from measurements of the Total Organic Carbon content in the feed water and the concentrate.

RESULTS AND DISCUSSION

In figure 3 the results of one of the experiments are presented. The figure shows the flux of the first ultrafiltration membrane at 500 kPa (5 bars) as a function of time. The results of the four tubul membranes arranged in series appeared to be identical, so that only the results of the first membrane are presented. Up to 22.5 hours the graph shows the situation where the ultrafiltration installation is f with demineralized, ultrafiltrated water. From 22.5 hours on feed wat consists of a solution of 167 mg/l PSL, having a MFI-value of 130,000 s/l2.

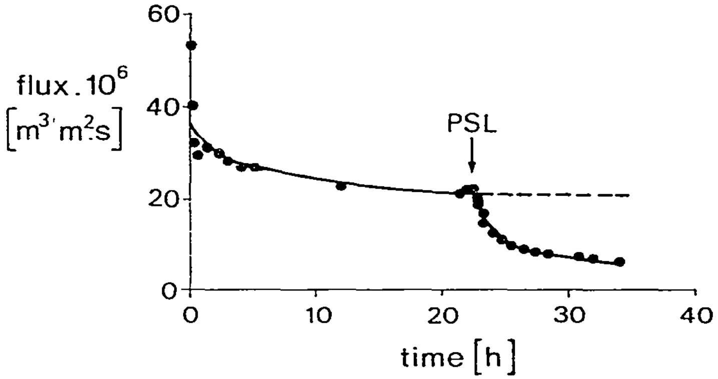

Fig. 3. Flux of ultrafiltration membrane fed with pure water and PSL-solution respectively at 500 kPa as a function of time.

Figure 4 illustrates the relative flux decline Δf as a function of time. In this figure also values calculated from equation (7) are given, assuming $\alpha = 1$ and $\beta = 1$. The conclusion is, that a good agreement exists between the measured and the calculated curve. The difference between the curves gradually decreases from 50 % in the beginning to zero. A number of other experiments showed smaller differences.

The difference between the curves in the beginning may be attribut to the occurrence of blocking filtration. The effect of blocking filtration is neglected in the mathematical model, so that lower valu of time are found to attain a certain flux decline value. The fact that the two curves converge may be ascribed to a decrease in deposition percentage during the run. The percentage of deposition measured, however, did not differ significantly from 100 %, but the Total Organic Carbon measurements were insufficiently accurate to justify a conclusion.

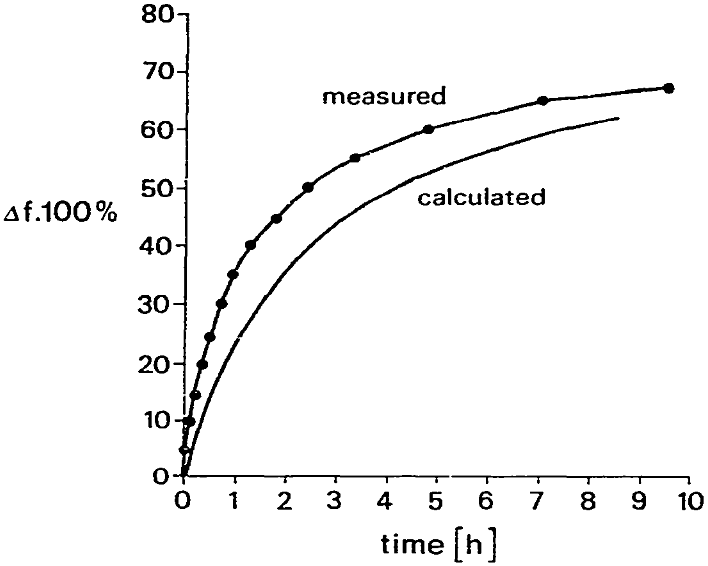

Fig. 4. Relative flux decline Δf as a function of time.

The assumption mentioned above is supported by the relation between $\frac{t}{V}$ and V, which is illustrated in figure 5. The slope of the

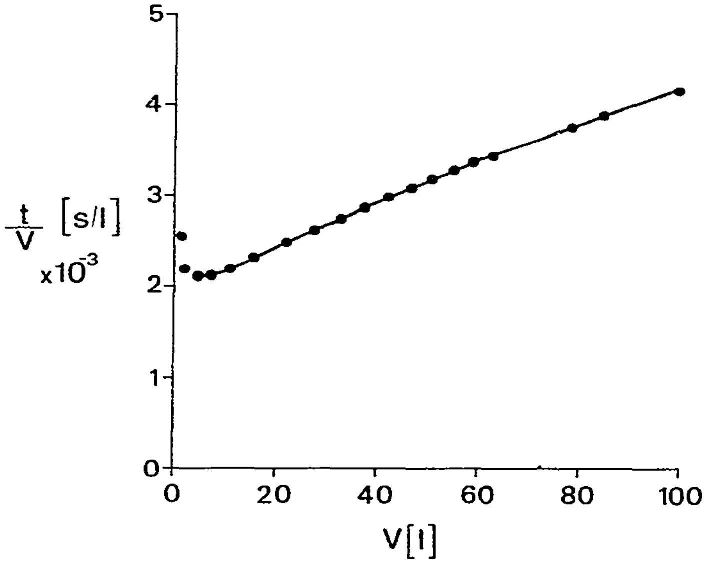

Fig. 5. Filtration curve of 167 mg/l PSL-solution with ultrafiltration membranes.

curve gradually decreases with time, which may be attributed to a decrease in α or β. A decrease in β is more likely, as a decreasing flux and an increasing thickness of the deposited layer enhance the chance of detachment of particles.

Another possibility to explain the differences mentioned is, that the MFI-value, contrary to theory, is pressure dependent. This possibility will be further researched.

ACKNOWLEDGEMENTS

The research in this paper was commisioned by the Netherlands Waterworks' Association and has partly been conducted within the framework of the cooperation between the Provincial Waterworks of North-Holland, Wafilin B.V. and the Netherlands Waterworks' Testing and Research Institute KIWA N.V.

REFERENCES

1 J.C. Schippers, H.C. Folmer and A. Kostense. The effect of pretreatment of river Rhine water on fouling of spiral wound reverse osmosis membranes. Proc. 7th Intern. Symp. on Fresh Water from the Sea, 2(1980)297-306.
2 J.C. Schippers and J. Verdouw. The Modified Fouling Index, a method of determining the fouling characteristics of water. Desalination, 32(1980)137-148.
3 G. Belfort and B. Marx. Artificial particulate fouling of hyperfiltration membranes-II. Analyses and protection from fouling. Desalination, 28(1979)13-30.
4 M.E. Woods, J.S. Dodge and J.M. Krieger. J. of Paint Techn., 40(1968)527.