

# Removal of humic substances by coagulation/hollow fibre membrane filtration

Av I. Machenbach, T. Leiknes and H. Ødegaard

Department of Hydraulic and Environmental Engineering,  
Norwegian University of Science and Technology

Innlegg på seminar 30. september 2002

**Abstract** Experiments were carried out to investigate the removal of humic substances from highly coloured raw water (50 µg Pt/L) by coagulation and outside-in hollow-fibre membrane filtration. Chitosan, a cationic biopolymer produced from crustacean shells, and polyaluminium chloride (PACl) were used as coagulants. The rate of permeability decline was determined for different backwash frequencies and different fluxes at a 95% water recovery of the membrane. Coagulation with PACl gave a good and consistent permeate quality with removals of 95.6%, 84.9%, and 66.1% for true colour, UV absorbers, and dissolved organic carbon (DOC), respectively. Longer filtration intervals with less frequent backwashing as well as lower specific aluminium dosages increased the rate of permeability decline. The particle size distribution in the retentate tank was not affected by the frequency of backwashing. Chitosan was less effective in coagulating humic substances and

the removal efficiencies were notably lower. Preliminary results suggest that the permeability declines somewhat faster for chitosan compared to PACl-coagulated water.

**Keywords** Chitosan, fouling, natural organic matter, polyaluminium chloride, ultrafiltration

## Introduction

Surface water is the drinking water source for 90% of the population in Norway. The typical water treatment plant receives lake water with a high concentration of natural organic matter (true colour between 30-80 mg Pt/L and DOC 3-8 mg C/L) but low in turbidity (<1 NTU), alkalinity (<0.5 meq/L), and hardness (<5 mg/L Ca) (Ødegaard, 1999).

Current Norwegian practice in membrane filtration of surface water is direct separation of NOM with membranes that have a nominal pore size in the range of 1.5-5.5 nm. In the majority of existing plants, spiral-wound modules housing hydrophilic

cellulose acetate or polyamide membranes are applied. Typical fluxes in NOM applications range between 12-17 L m<sup>-2</sup> h<sup>-1</sup> at operating pressures between 3-6 bar. Among the disadvantages are the low practically feasible water recovery (about 75%), high energy dissipation (0.2-0.8 bar m<sup>-1</sup>), and rapid accumulation of foulants, which requires a daily chemical cleaning cycle. Thorsen (2000) found that particles in the range of 0.2-3 µm need to be removed to alleviate the fouling problem. Many studies aim therefore at pre-treatment by coagulation to control fouling (Carrol *et al.*, 2000; Peuchot and Ben Aïm, 1992; Lahoussine-Turcaud *et al.*, 1990).

Submerged hollow-fibre systems have been applied successfully in drinking water applications in recent years (Côté *et al.*, 1998). Applying ultrafiltration membranes with larger pores allows operation at higher fluxes but chemical pre-treatment is required to achieve sufficient NOM removal. The correct choice of coagulant and operating conditions is essential to control fouling.

The objective of this study is to investigate coagulation/flocculation of highly coloured surface water with outside-in hollow-fibre UF membranes in a submerged membrane reactor configuration. As coagulants polyaluminium chloride, chitosan, and cationic synthetic polymers are applied. Pilot-scale experiments are conducted at 95% water recovery to minimize the concentrate volume for disposal. The parameters of interest include permeate quality, fouling

development, as well as backwashing/cleaning efficiency.

## Experimental

### Raw water

Reconstituted raw water with a colour of 50 mg Pt/L (pH 7) was prepared from tap water by adding a humic concentrate. Trondheim tap water is calcinated water from Lake Jonsvatnet with a natural colour of about 12-13 mg Pt/L. The humic concentrate was an eluate from a nearby water works where anion exchange is used as the NOM removal process. The reconstituted raw water had a DOC concentration of 6.1 ± 0.25 mg C/L and a UV<sub>254</sub>-absorbance of 31.1 ± 1.1 m<sup>-1</sup>.

### Coagulants

The coagulants used in this study were

- Polyaluminium chloride (PAX-16, aqueous solution containing 8.05% wt Al, Kemira Chemicals AS)
- Chitosan (ChitoClear™, degree of deacetylation 94%, Primex Ingredients ASA)

### Jar-tests

Preliminary coagulation tests in 1-L glass jars were carried out to estimate the removal efficiencies for colour, UV absorbing compounds, and DOC as a function of coagulant dose. The raw water pH was adjusted to pH 6.3 ± 0.1 in tests with polyaluminium chloride (PACl) and to pH 5 in tests with chitosan. Coagulants were added during rapid mixing at a paddle speed of 400 rpm. After one minute of rapid mixing and a 15-minute flocculation

period at a paddle speed of 30 rpm, the coagulated suspension was settled for 30 minutes. Samples were drawn just below the water level and filtered using a 0.2- $\mu\text{m}$  PES membrane filter.

### Continuous membrane experiments

The flowsheet of the membrane

plant is shown in Fig. 1. Acid (hydrochloric) and coagulant were dosed using high-intensity inline mixers. The coagulated humic water was flocculated in a pipe flocculator at high G-value ( $400 \text{ s}^{-1}$ ) for 30 sec to achieve rapid microfloc aggregation.

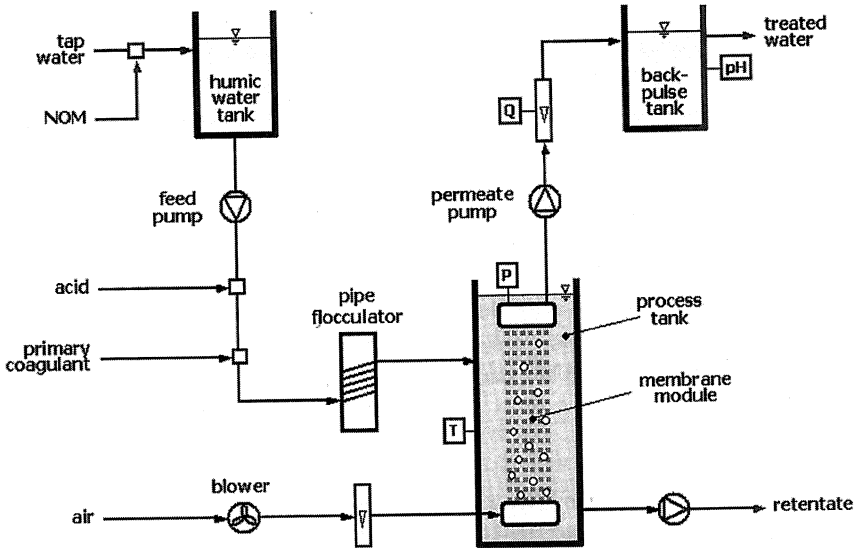


Figure 1 Flowsheet of membrane pilot unit

A submerged Zenon ZW-10 module containing UF hollow-fibres with a nominal pore size of 40 nm and a total membrane surface area of  $1 \text{ m}^2$  was used. The module was submerged in a 20-L cylindrical retentate tank and operated in outside-in mode at constant flux. During backwash, air was introduced into the retentate tank through diffusers in the bottom of the module at a constant airflow rate of  $5.1 \text{ m}^3/\text{h}$  (air scouring). The operating pressure, the temperature in the retentate tank, and the permeate flowrate

were recorded continuously using a data acquisition system.

Before each experiment, the membrane was backwashed from the permeate side with a sodium hypochlorite solution. After a 24-hour soak period, the module was rinsed with distilled water. In general, the clean membrane permeability was restored after chemical cleaning.

For the first hours of each experiment, the membrane was operated in dead-end mode to attain the steady-state suspended solids concentration

in the retentate tank. Assuming that the tank is filled with the coagulated suspension on start-up, the time,  $t^*$ , to reach steady-state conditions is given by

$$t^* = \frac{\phi}{100 - \phi} \frac{V_t}{Q_p} \quad (1)$$

In Eq. (1)  $\phi$  denotes the water recovery (%),  $V_t$  the process tank volume, and  $Q_p$  the permeate flowrate. Thereafter, retentate was withdrawn continuously to obtain a 95% water recovery. The experiment was stopped after 48 hours of operation.

Fouling was evaluated by the decline of the instantaneous membrane permeability during the course of an experiment. The membrane permeability,  $L$ , is defined as

$$L = \frac{J}{\Delta P} = \frac{Q_p}{A \Delta P} \quad (2)$$

where  $L$  represents the permeability,  $J$  the flux,  $\Delta P$  the transmembrane pressure,  $Q_p$  the permeate flowrate, and  $A$  the membrane surface area.

According to Darcy's law the flux,  $J$ , through a membrane is given by

$$J = \frac{\Delta P}{\eta \sum_i R_i} \quad (3)$$

where  $\eta$  is the water viscosity and  $R_i$  the resistance in series, such as membrane resistance and resistances due to fouling. Eq. (3) allows correcting the transmembrane pressure,  $\Delta P$ , for temperature effects.

The instantaneous permeability was calculated according to Eq. (2) using

the transmembrane pressure measured immediately after permeate backpulsing (normalized to 20°C). After reaching steady-state conditions, the permeability decline was linear and the rate of decline was determined by regression.

## Analytical methods

Dissolved organic carbon (DOC) was determined using a Tekmar Dohrmann Apollo 9000 TOC analyzer. Raw water samples were passed through a 0.45- $\mu\text{m}$  Sartorius cellulose nitrate filter prior to analysis to remove particulate matter.

True colour and UV-absorption were determined on a Hitachi U-3000 UV/Vis spectrophotometer. Colour was determined by measuring the absorbance of a 0.45- $\mu\text{m}$  filtered sample at 410 nm in a 5-cm cell. UV absorption was determined at a wavelength of 254 nm using a 1-cm quartz cell.

Residual aluminium in permeate samples was analyzed by inductively coupled plasma-mass spectrometry (HR-ICP-MS). The particle size distribution in retentate samples was determined by laser diffraction spectroscopy (Beckman Coulter LS230). Zeta-potential was analyzed by laser Doppler velocimetry on a Coulter 440SX.

## Results and discussion

### Jar-tests

Coagulation tests with PACl revealed that a specific aluminium dosage of 5 mg Al/L removes 94% of true colour, 85% of UV-absorbing compounds, and 63% of DOC (Fig. 2). Although

removal of colour and UV-absorbers did not increase much from 4 to 5 mg Al/L, the latter dosage was taken as optimal dosage to ensure charge neutralization.

Coagulation with chitosan increases the DOC upon addition to raw water (a 1 mg/L chitosan solution has a DOC concentration of about 0.67 mg C/L). Up to a dosage of 2 mg/L chitosan, no floc formation was visible and the 0.45- $\mu$ m membrane filter retained only marginal amounts of

aggregates. Removal of colour and UV-absorbers increased with increasing chitosan dosage but removal efficiencies were notably lower than for PACl. In the investigated dosing range, no optimal chitosan dosage was found. At all chitosan dosages a positive zeta-potential was measured. For the pilot experiments on the membrane unit, a dosage of 5 mg/L was chosen to be able to compare results with other ongoing experiments.

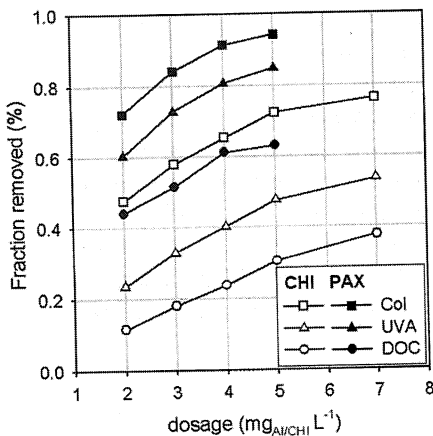


Figure 2a Removal of Colour, UVA254 and DOC from jar-test experiments (open symbols denote chitosan values, closed symbols for PACl values)

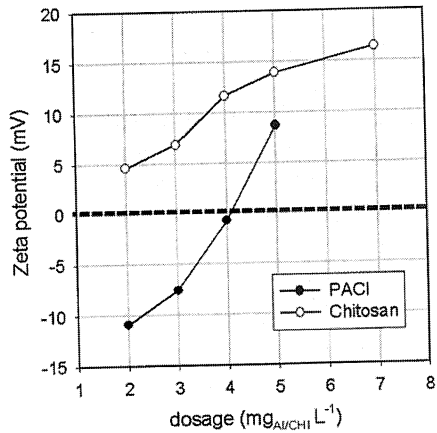


Fig. 2b Zeta-potential as a function of coagulant dose

### Membrane filtration of PACl coagulated water

The permeate quality was consistent during each experiment and depended on the PACl dose. Removal efficiencies were significantly better than the estimated results obtained in jar-tests (Tab. 1), which can be attributed to the lower cut-off of the membrane and the optimized coagulation/flocculation

conditions.

Residual aluminium in permeate samples never exceeded 30  $\mu$ g Al/L and did not increase significantly over the concentration in the raw water. Hence, the membrane removed colloidal aluminium aggregates efficiently. The turbidity measured in permeate samples was below 0.1 NTU in all analyzed samples.

Parameter	Permeate		Removal	
	3.8 mg Al/L	5 mg Al/L	3.8 mg Al/L	5 mg Al/L
True Colour (mg Pt/L)	4.1 (0.3)	2.2 (0.4)	91.7 %	95.6 %
UVA <sub>254</sub> (m <sup>-1</sup> )	6.6 (0.4)	4.7 (0.5)	78.7 %	84.9 %
DOC (mg C/L)	2.6 (0.2)	2.1 (0.2)	58.7 %	66.1 %

Standard deviations in parentheses

Table 1 Permeate quality after coagulation/flocculation with polyaluminium chloride (PACl)

Cake formation was visible on the membrane surface during filtration. The combined effect of backwashing and air scouring removed cake-fouling layers from the membrane surface. After steady-state conditions prevailed in the retentate tank, the loosened cake particles were up to 1-2 mm in size and settled rapidly.

The suspended solids concentration in the retentate tank influenced the pressure increase during the filtration interval. During the dead-end phase, the pressure increase during the filtration interval increased with the suspended solids concentration. After backwashing/air scouring, the operating pressure returned nearly to its initial value.

Fouling was investigated with respect to length of filtration interval, flux, and coagulant dosage. The length of the filtration interval influenced the rate of permeability decline notably. During a 30-min cycle (29 min 30 s filtration and 30 s backwash), the permeability decline was lower than in a 60-min cycle (59 min 30 s filtration and 30 s backwash). This effect was apparent for both applied fluxes of 60 and 75 L m<sup>-2</sup> h<sup>-1</sup>. Furthermore, the rate of permeability decline increased with increasing flux during a 30-min cycle. Although this effect was not evident in the 60-min cycle it must be noted that a comparatively high standard deviation was obtained at a flux of 60 L m<sup>-2</sup> h<sup>-1</sup> (Tab. 2).

Flux (L m <sup>-2</sup> h <sup>-1</sup> )		Rate of permeability decline (L m <sup>-2</sup> h <sup>-2</sup> bar)	
Filtration	Backwash	30 min cycle	60 min cycle
60	90	-0.53 (0.09)	-1.34 (0.21)
75	100	-0.76 (0.07)	-1.19 (0.08)

\* 30 sec backwashing

standard deviations in parentheses

Table 2 Permeability decline at different fluxes and filtration intervals (dosage 5 mg Al/L)

At a lower specific aluminium dose (3.8 mg Al/L), the permeate quality was still satisfactory. However, the rate of permeability decline obtained in a 30-min cycle at a flux of 75 L m<sup>-2</sup> h<sup>-1</sup> amounted to -1.76 L m<sup>-2</sup> h<sup>-2</sup> bar (0.09) and was thus significantly higher than at the optimal dosage of 5 mg Al/L.

### Membrane filtration of chitosan coagulated water

In our research group we have obtained good results with chitosan as coagulant

in contact-filtration experiments (Eikebrokk and Saltnes, 2000). Colour removal in these experiments compared well to results obtained in earlier studies with similar raw water. The hollow-fibre membrane did retain organic aggregates but the DOC removal was rather low with about 30% (Tab. 3). Consequently, a low removal of UV-absorbing compounds was measured. Higher chitosan dosages might be required to improve the permeate quality. The turbidity in permeate samples never exceeded 0.1 NTU.

Parameter	Permeate	Removal
True Colour (mg Pt/L)	15.3 (0.9)	69.6 %
UVA <sub>254</sub> (m <sup>-1</sup> )	16.0 (0.7)	42.8 %
DOC (mg C/L)	4.2 (0.3)	30.2 %

Standard deviations in parentheses

Table 3 Permeate quality after coagulation/flocculation at pH 5 with chitosan (dose 5 mg/L)

The results shown in Tab. 3 were obtained at a flux of 75 L m<sup>-2</sup> h<sup>-1</sup> and a cycle time of 30 minutes. At this stage, evaluation of the rate of permeability decline is still somewhat inconclusive but preliminary results suggest that the membrane is fouled at a higher rate compared to PACl.

### Particle size distributions in retentate tank

During the filtration cycle, suspended solids settled in the retentate tank. Air scouring resuspended the settled solids whenever the membrane was backwashed. Retentate samples were drawn 10 cm below the water level shortly after backwashing and the particle size distribution was determined.

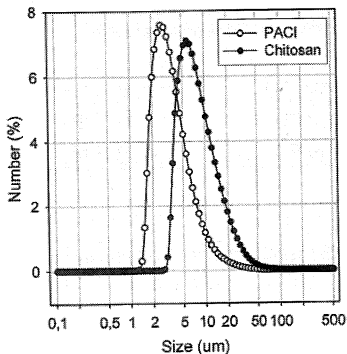


Figure 3a Differential particle size distribution (retentate PACl and chitosan)

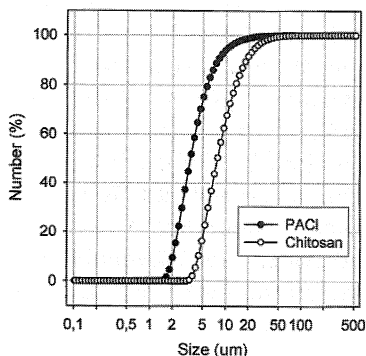


Figure 3b Cumulative particle size distribution (retentate PACl and chitosan)

The frequency of backwashing did not affect the particle size distribution in the retentate when PACl was used as coagulant. Fig. 3a shows the typical distribution that was obtained repeatedly. Coagulation with chitosan produced somewhat larger particles as can be seen in Fig. 3b.

## Conclusions

- Jar-tests experiments were used to determine the optimal coagulant dose. The removal efficiencies of the hollow-fibre membrane were significantly better which can be attributed to the lower cut-off of the membrane and the optimised coagulation conditions.
- The permeate quality was consistent in all experiments. Minor variations in the removal efficiencies were most likely due to variations of flow and dosage in the coagulation system. The permeate turbidity was below 0.1 NTU in all analysed samples.
- In experiments with PACl as coagulant, shorter filtration intervals at a flux of  $60 \text{ L m}^{-2} \text{ h}^{-1}$  (more frequent backwashing) reduced

the rate of permeability decline. This effect was not evident at a flux of  $75 \text{ L m}^{-2} \text{ h}^{-1}$  where the permeability declined faster.

- At a PACl dosage below charge neutralization, a significantly higher rate of permeability decline was obtained although the permeate quality remained satisfactory.
- The permeate quality after chitosan coagulation was consistent but unsatisfactory.
- Preliminary results suggest that the rate of permeability decline is higher with chitosan compared to PACl.
- The frequency of backwashing did not affect the particle size distribution in the range between 0.1-10 µm when PACl was used as coagulant.

## References

- Carroll, T., Vogel, A., Rodig, A., Simbeck, K. and Booker, N. (2000). Coagulation-microfiltration processes for NOM removal from drinking water. In: *Chemical Water and Wastewater Treatment VI*, H. Hahn, E. Hoffmann, H. Ødegaard (eds.), Springer, Berlin, 171-180.



Côté, P., Mourato, D., Güngerich, C., Russel, J. and Houghton, E. (1998). Immersed membrane filtration for the production of drinking water: Case studies. *Desalination*, 117(1-3), 181-188.

Eikebrokk, B. and Saltnes, T. (2000). NOM removal from drinking water by chitosan coagulation and filtration through light-weight expanded clay aggregate filters. Proc. *Innovations in Conventional and Advanced Water Treatment Processes*, Amsterdam, The Netherlands, 26-29 September 2000.

Lahoussine-Turcaud, V., Wiesner, M., Bottero, J. and Mallevialle J. (1990). Coagulation pretreatment for ultrafiltration of a surface water. *Journal American Water Works Association*, 82(12), 76-81.

Peuchot, M. and Ben Aïm, R. (1992). Improvement of crossflow microfiltration performances with flocculation. *Journal of Membrane Science*, 68(3), 241-248.

Thorsen, T. (2000). Fundamental studies on membrane filtration of coloured surface water. Dissertation, Department of Hydraulic and Environmental Engineering, Norwegian University of Science and Technology, Trondheim, Norway.

Ødegaard, H., Eikebrokk, B. and Storhaug, R. (1999). Processes for the removal of humic substances from water – An overview based on Norwegian experiences. Proc. *IAWQ-IWSA Joint Specialist Conference on Removal of Humic Substances from Water*, Trondheim, Norway, 24-26 June 1999.