Ozonation/biofiltration for NOM-removal by using the rotating disc membrane filtration system

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Innlegg på seminar 30. september 2002

Abstract. Surface waters containing humic substances (NOM) represent a problem in many countries because it gives the water a brownish colour and NOM are precursors for halogenated organic compounds as well. Removal of humic substances is normally carried out by coagulation processes, sorption processes or membrane processes (nano filtration). Another option that is basis for this paper is ozonation/biofiltration. The method is based on the fact that ozonation removes colour but creates more easily biodegradable organic matter that has to be removed in a subsequent biological reactor. The paper refers to experiments with different biofilters, but deals specifically with the use of a rotating disc membrane filtration system. Experiments are reported in which the rotating disc membrane reactor was used both as the bioreactor as well as the separation reactor of the ozonation/biofiltration process..

Key words: Ozonation, biofiltration, rotating membrane filtration reactor

Introduction

One of the major problems of using surface water as the water source in northern climates is high content of humic substances, also referred to as natural organic matter (NOM), resulting in high colour and total organic carbon (TOC) content. Removal of NOM is required since coloured water is unattractive to consumers, results in colouring of clothes during washing, can cause odour and taste and increases corrosion in distribution network. NOM also lead to formation of disinfection by-products when water is chlorinated. Halogenated compounds resulting from chlorination of drinking water has been a major concern since their discovery in early 1970's. Since then, a large amount of research has been done to minimize their formation in drinking water because some of the chlorination by-products are carcinogens. One possibility is to eliminate the chlorination step in water treatment and use alternative disinfection methods. Use of ozone as the primary disinfectant is increasing. It is also an efficient treatment process for removing colour and, combined with a biofiltration step, organic matter (Ødegaard, 1996).

This is because ozone increases the biodegradability of water. Since the presence of biodegradable organic carbon in drinking water can cause regrowth problems in the distribution network, biologically active filters are used to remove the biodegradable fraction from the ozonated water. This is the basis for the treatment in ozonation/biofiltration plants for which the principle is shown in Figure 1.

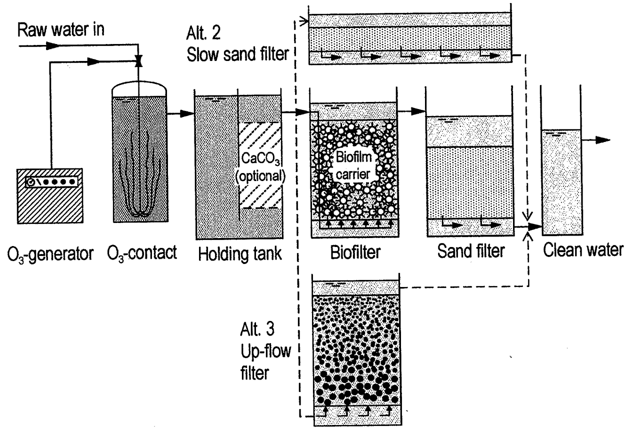


Figure 1 Flow diagram for alternative versions of an ozonation/biofiltration plant

Ozone is added to the water ahead of a contact column. The colour is reduced and more easily biodegradable organic matter is formed. Reduced compounds as iron and manganese is oxidized as well and precipitated. The relatively high ozon dosage required will lead to very efficient disinfection. Residual ozone can be exhausted in a holding tank (as shown in the figure) or by letting the water pass a coal-containing filter medium (activated carbon or anthracite) that will catalytically convert residual ozone to oxygen. Since ozonation results in a pH-drop, a calcium-carbonate filter may be placed in the holding tank if needed for pH-control in extremely low alkalinity water. Normally this is not necessary.

The water is then lead to a filter, the biofilter, in which the newly formed easily biodegradable organic matter is biodegraded. Most ozonation/biofiltration plants in the world, use activated carbon as biofilter medium, thus combining adsorption and biofiltration. This method has not been found economically competitive for humic waters in Norway (Ødegaard et al, 1986). In our group, various filter media have been tested in various filter configurations (Ødegaard, 1996, Melin and Ødegaard, 2000, Melin and

Ødegaard, 2002), such as biofilter with plastic carriers followed by sand filtration (single or dual media), combined biofilter and separation filter by use of a slow sand filter (alt 2 I Figure 1) or by use of upflow expanded clay aggregate (Filtralite) filter (alt. 3 in Figure 1).

Lately we have investigated biofiltration and biomass separation by the use of the rotating membrane system, inspired by the work of Kimura (2000) that used the same system for nitrification of river water. The idea behind this is the fact that the biomass production, as a result of the biodegradation, is so small that separation direct on membrane filters could be feasible. Before going into the details of this research, however, some background information of the whole ozonation/biofiltration process shall be given.

Design and operation of ozonation/biofiltration plants

The ozonation step

The ozone dosage is primarily dependent on the final colour aimed for in the water. A model that has been found to fit the measured results quite well is shown in Figure 2: $\mathbf{c/c_0 = 1/(1+20\ D/c_0)}$, where c and c_0, are colour (mg Pt/l) in raw and ozonated water respectively and D is the ozone dosage (mg O_3/l)(Fløgstad and Ødegaard, 1985). The dosage given by this model is typically equivalent to1.0 g O_3/g $TOC_{raw\ water}$ or 0.15 mg O_3/mg $Pt_{raw\ water}$. This results in dosages far higher that those needed for bacteria and virus disinfection. Giardia will also be killed while even higher dosages will be needed to eliminate *Cryptosporidium.*

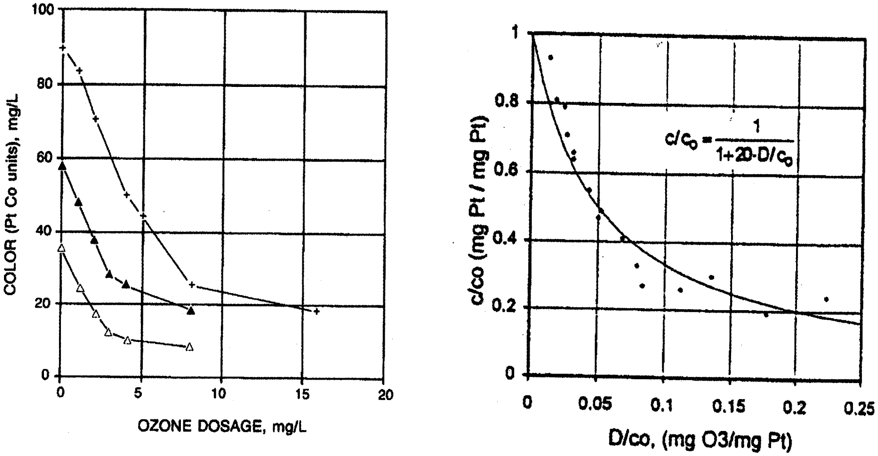


Figure 2. Colour removal by ozonation (Fløgstad and Ødegaard, 1985)

The increase of the biodegradable fraction in water depends on the water source and ozone dosage (Carlson and Amy, 1997). The reaction of ozone with NOM increases the concentrations of some low molecular weight compounds which are easily biodegradable. Low molecular weight compounds identified from ozonated water include aldehydes, ketones, ketoacids and carboxylic acids (Glaze *et al.*, 1989; Carlson and Amy, 1997; Melin and Ødegaard, 2000). In Figure 3 it is demonstrated that there exist a stoiciometry between formation of the various ozonation products and ozonation dosage.

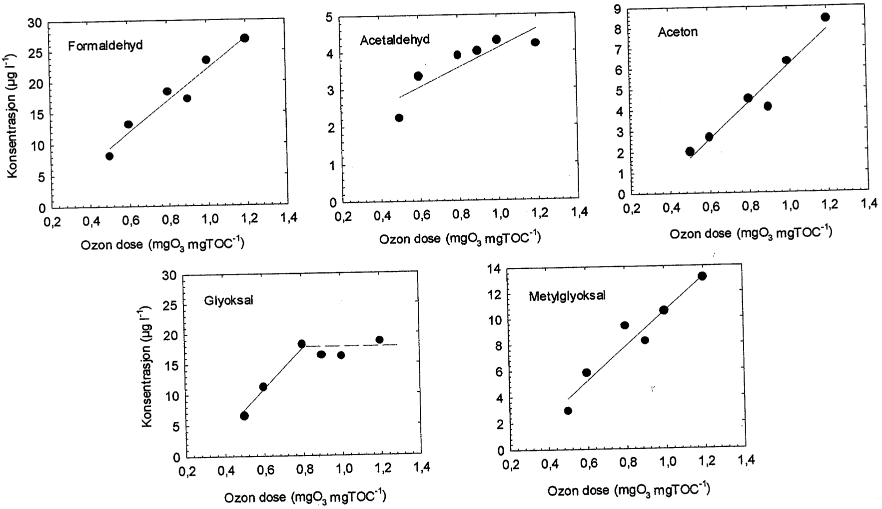


Figure 3. Formation of aldehydes and keto acids upon ozonation of NOM water (Melin and Ødegaard, 2000)

The biofiltration step

Biofilter studies with various filter media have demonstrated that the empty bed residence time (EBCT) seems to be of greater importance than the type of filter media used. The choice of filter medium should therefore more be based on its efficiency to separate biomass and other particles than on its suitability for biodegradation. Generally it has been demonstrated that the EBCT needed in the biofilter is in the range of 15-25 min. The removal of ozonation by-products could be described well by a 1'st order model in a plug flow reactor (Melin and Ødegaard, 2000).

$$S_{out} = (S_{in}-S_{min}) \cdot e^{-k\theta} + S_{min}$$

Where θ is the empty bed contact time (min), k is the first order rate constant (min^{-1}), $S_{in,out}$ is inlet and outlet concentrations respectively (µg/l) and S_{min} is the lowest substrate concentration that can sustain growth (µg/l).

The rate constant (k) will be dependent upon time of operation since biomass will increase between each backwash of the filter. In figure 4 is the sum concentration of the ozonation by-products from a biofilter 1 day and 21 days after backwash (points) shown as well as model calculations (lines). It is demonstrated that the rate of degradation is higher at 21 days, but even immediately (1 day) after filter backwash, the rate is so high that there is no use in increasing the EBCT over 15 min. It is relatively little TOC that is removed, typically in the range of 20-30 %. It can be stated, therefore, that it is more significant what kind of TOC (the readily biodegradable) that is removed than how much TOC that is removed.

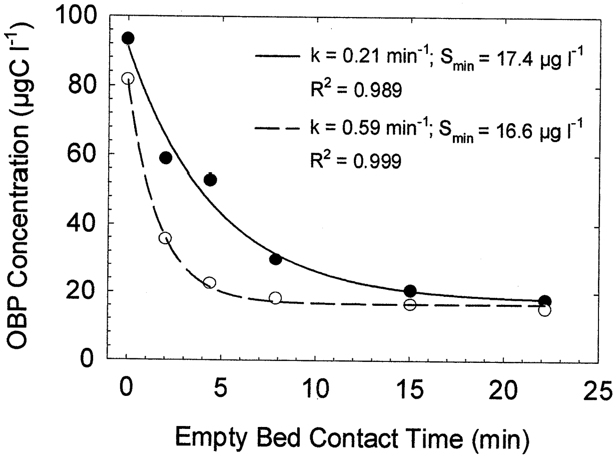


Figure 4. The influence of EBCT on the concentration of the sum of ozonation by-products (OBP measured as µg/l) in the treated water after 1 day (•) and 21 days (o) after filter backwash. Filtration rate v_f=5.1 m/h)

The separation step

The separation step has two purposes; a) to separate the biomass that is formed during biodegradation and b) to separate particles that are entering the plant via the raw water or that is produced during the process because of oxidation/precipitation. The latter is totally dependent upon raw water quality. In typical Norwegian lake waters, low in turbidity, the contribution from the raw water is low. Some iron and manganese will be oxidized and precipitated.

The production of biomass is very small. If TOC in the order of 1 mg/l is biodegraded, the biomass production will be in the order of only 1-2 mg SS/l. This means that the filter head-loss build up in the filter is very small and that long filter run times can be expected. Filter run time will obviously be dependent on the filter medium. Filters with plastic biofilm carriers need to be backwashed very seldom (every 2-3 months) while finer media filters (expanded clay aggregates, anthracite, activated carbon, sand etc) will need to be backwashed every 2-4 weeks. We have observed the following head-loss rates for various types of filters:

- Single media sand filter (75 cm, 0.4-0.8 mm) at 2 m/h : 3-4 cm/d
- Dual media anthracite (d_{10} =1,0 mm, U_{max} =1,4)/sand (d_{10} =0,4 mm, U_{max} =1,4), (75 cm- 45+20) at 5 m/h : 1-2 cm/d
- Upflow expanded clay aggregate filter (175 cm, 0.5-2.5 mm): 2 cm/d at 5 m/h and 4 cm/d at 10 m/h.

Ozonation/biofiltration by using the rotating membrane filtration system

Kimura (2000) proposed a membrane biofilm reactor based on the rotating membrane filtration system manufactured by Hitachi Plant Ltd in Japan. The principle of the system is shown in Figure 5. The water to be membrane filtered is lead into a reactor chamber in which rotating discs covered with membranes are placed on a rotating shaft. The water passes the membrane and sucked out of the unit by a collection system is the discs and well as in the shaft. The standard membrane used is a 750.000 Dalton ultrafiltration membrane.

The basic idea of Kimura (2000) when using this membrane unit for removal of ammonium in river water, was to let nitrifiers grow in the membrane chamber, primarily on the membrane itself and separate the biomass by the membrane. He tested out various ways to control fouling of the membrane, i.e. the transmembrane pressure (TMP) build up, such as increased rotational speed, chemical cleaning etc.

Kimura found that a very efficient way was to add small sponges in the membrane reactor chamber. These sponges controlled the biomass layer on the membrane in such a way the run times between chemical cleaning could be increased significantly.

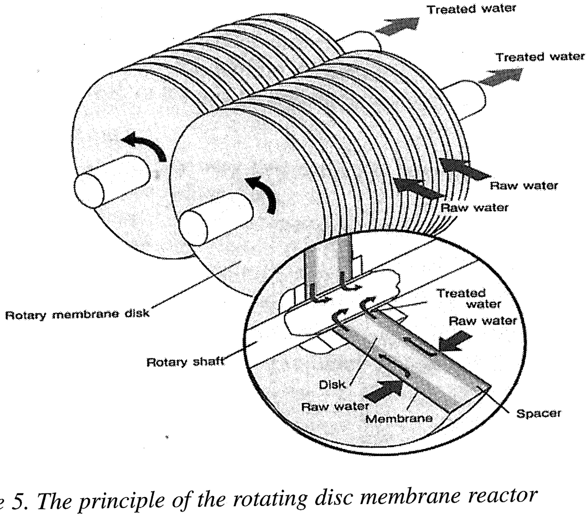


Figure 5. The principle of the rotating disc membrane reactor

Our idea was to utilize the same principle for ozonation/biofiltration of humic water since biomass production here could be expected to be of the same magnitude as the one Kimura experienced. The project has been carried out in steps and is not yet finished, but some results will be presented here.

The pilot plant

The principle of the pilot plant is shown in Figure 6.

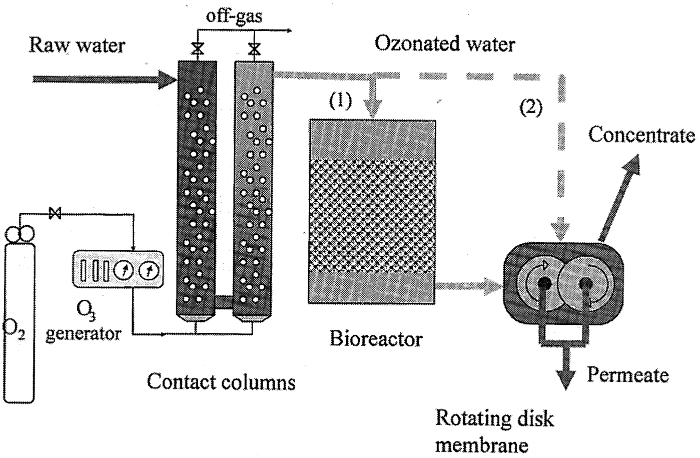


Figure 6. The principle build-up of the pilot plant

Raw water (which was tap water with at natural humic concentrate added to give a colour of 50 mg Pt/l, UV-absorbance of 25 Em^{-1} and TOC of 6 mg/l), was lead through two open serial coupled glass contact columns (total contact time: 16 min) to which ozone was added (ozone generated by a Sander laboratory ozonizer). After passing a 50 l holding tank (EBCT=30 min, not shown in the flow diagram) in order to exhaust residual ozone, the ozonated water could either be lead through a biofilter (packed with Kaldnes K1 biofilm carriers, EBCT: 30 min) and thereafter lead to the rotating disc membrane unit, or it could be lead directly to the membrane unit

The experiments carried out

Some introductory experiments were first carried out to determine the influence on TMP of clean water fluxes and rotational speed of the discs.

Thereafter the unit was operated on ozonated water for about 1800 hrs during which various operational modes were tested out. During the first 1200 hrs or so, the water introduced to the membrane unit was first lead through the biofilter, while it was lead directly to the membrane unit after ozonation later. Sponges were introduced to the membrane unit chamber after about 900 hrs of operation. Four operational periods with dead-end filtration (at four different fluxes) where carried out first and then two cycles with a recovery of less than 100 % (89 % and 67 %) were carried out.

Experimental results

In Figure 7 is shown the transmembrane pressuse (TMP) as function of flux and disc rotation when operated on clean (distilled) water. Six rotation at speeds were investigated (0, 50, 100, 200, 300, and 340 rpm) and in each step the TMP was determined at three different fluxes.

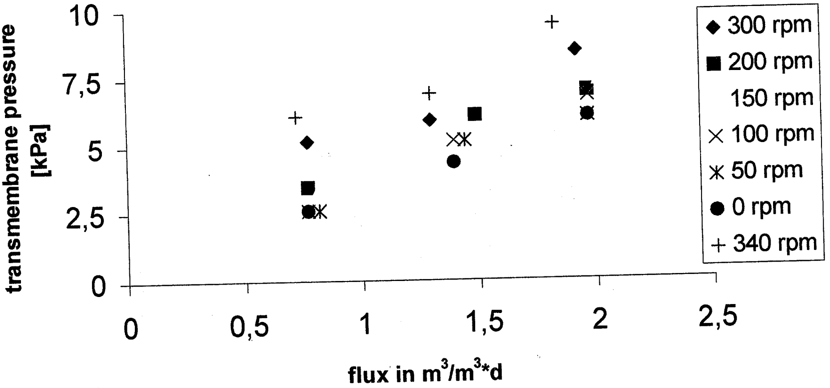


Figure 7. Transmembrane pressure as a function of flux and rotation in clean (distilled) water

Figure 7 shows that TMP increases close to linearly with increasing flux and that it also increases with rotational speed at a given flux. It could be demonstrated that the TMP increase as function of rotational speed turned from a linear function into a power function between 200 and 300 rpm. Due to strengthened centrifugal forces throughout rotation the water is pushed away from the disc-surfaces. As a result of this effect the suction pump has to maintain a higher suction pressure to uphold the current flux. In practice, however, a rotational speed higher than 200 rpm will be too energy demanding and costly. Additionally, a higher basic pressure shortens the time in between membrane cleaning intervals.

In the rest of the experiments the rotational were kept at 50 rpm during filtration and increased to 350 rpm during membrane cleaning (self cleaning by shear). When sponges were introduced to improve cleaning, the plant was operated without rotation of the discs except when sponge cleaning was used. Then a rotational speed of 150 rpm, that ensured full mixing of the sponges in the reactor chamber, was implemented.

In Figure 8 is shown the removal of colour over the whole experimental period. The colour removal is primarily dependent upon the ozone dosage and as demonstrated, the dosage of about 1 mg O_3/mg $TOC_{raw\ water}$, resulted in a clean water colour of about 10 mg Pt/l and removal of around 80% which is typical for ozonation/biofiltration plants.

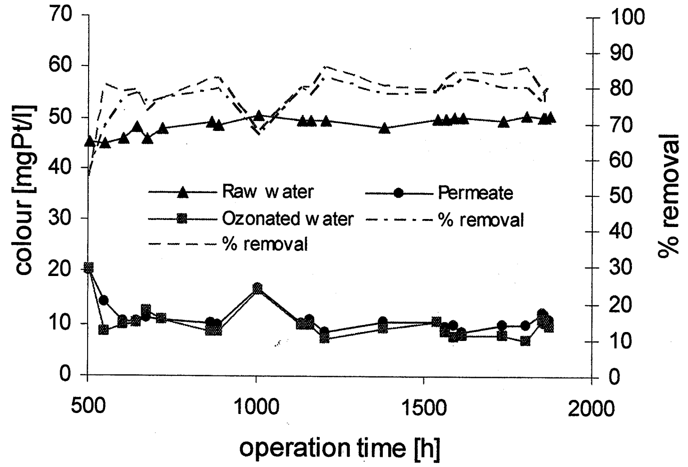
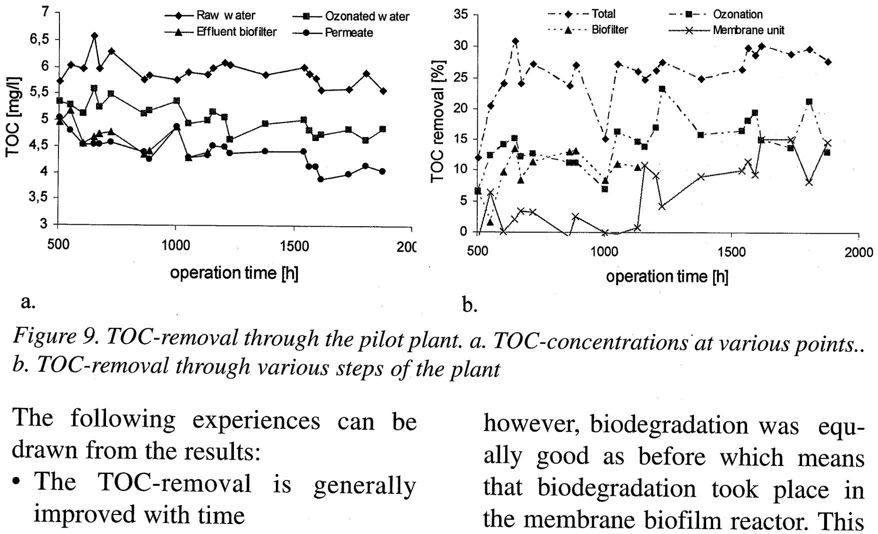


Figure 8. Removal of colour during the whole experimental period

In Figure 9a is shown the concentration of TOC in various places of the plant and in Figure 9b the TOC-removal that took place in each of the treatment steps.



a.

b.

Figure 9. TOC-removal through the pilot plant. a. TOC-concentrations at various points.. b. TOC-removal through various steps of the plant

The following experiences can be drawn from the results:

- The TOC-removal is generally improved with time
- The membrane separation itself had little impact on TOC-removal in the period when the water was biofiltered prior to the membrane unit. After biofiltration was terminated, however, biodegradation was equally good as before which means that biodegradation took place in the membrane biofilm reactor. This is well demonstrated in Figure 10b where it is shown that TOC-removal in the membrane unit is picking up after about 1100 hrs (when pre-biofiltration was termi-nated).

- Also ozonation as such removes TOC – about to the same degree (around 15 %) as biodegradation. It seems, however, that TOC-removal by biodegradation in the membrane unit was still on the rise when the experiments were temporarily terminated.

In Figure 10 is shown the development of TMP during the whole experiment. In the start the membrane unit was operated at a flux of 0.5 m/d (21 l/m²h). Due to fouling the TMP increases with time. When increasing the flux to 0.72 and 0.96 m/d respectively, the rate of TMP increase (slope of line) increased quite dramatically.

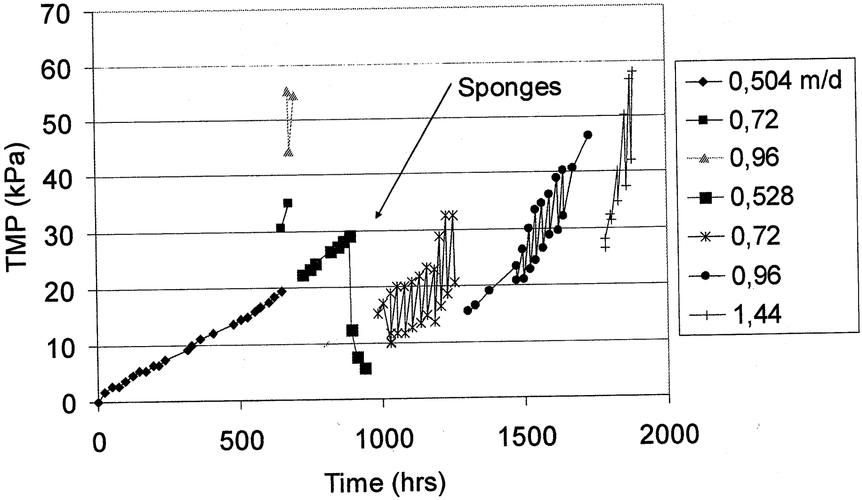


Figure 11. Development of TMP throughout the whole experimental period

When lowering the flux once again to around 0.5 m/d the slope of the TMP increase was brought down to its original level. Remember that this was the period when cleaning of membrane was carried out by self cleaning (increased rotational speed of discs to 350 rpm for 15 min) only.

After about 850 hrs of operation, sponge cleaning was introduced. Terui (2002) has found that the optimal sponge size is 60-65 % of the space between two membrane discs. Optimal cleaning was obtained when the sponges filled 0.5 % of the membrane tank. We used sponges made from polyurethane that were ca. 3.5 times 3.5 mm that filled about 500 ml. 150 rpm were found to be the rotational speed where all polyurethane cubes were in motion and seemed to be mixed up evenly in the chamber.

Sponge cleaning was first carried out for 24 h of rotation (at 150 rpm) that brought the TMP down from a pressure of 24 kPa to 6kPa. After this the plant was operated without rotation of the discs for three days and the TMP increases relatively fast again. But after three days of operation the

TMP was 17 kPa still 7 kPa below the 24 kPa initial pressure. Therefore a much better cleaning effect after the addition of sponges than after mere rotation was experienced.

The intention was now to run the plant with low speed rotation (50 rpm) and continuous sponge cleaning. However, due to a misunderstanding the student who operated the plant, continued operation with no rotation during filtration, but sponge cleaning once a day (10 min at 150 rpm). The flux was also increased in three steps (0.72 m/d, 0.96 m/d and 1.44 m/d). It is demonstrated that the rate of TMP increase at 0.72 m/d and 0.96 was much lower than it was without sponge cleaning, but the rate of TMP increase was still strongly influenced by the flux.

Influence of recovery

Towards the end of the experiment, we wanted to analyse the influence of reduced recovery as compared to the 100 % recovery (dead end) that we had operated the plant under before. The results of this experiment are shown in Figure 11. The plant was operated at a high flux (1.44 m/d) and between each experiment (for each recovery, 100%, 89 % and 67%), a 30 min sponge cleaning was carried out. Recovery was reduced by draining portions of water from the membrane chamber.

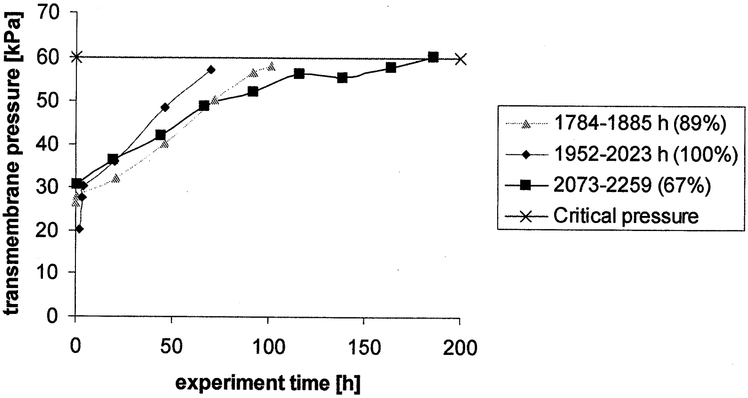


Figure 11. Effect of recovery on TMP development at a flux of 1.44 m/d.

It is demonstrated that while we reached the critical TMP (of 60 kPa) after about 70 hrs of operation, this could be increased to more that 100 hrs at 89 % recovery and 180 hrs at 67 % recovery.

Future work

We find that the results from the experiments are quite encouraging and shall continue. We shall concentrate more on optimal operational strategy. For instance will we investigate how continuous operation with sponges present will influence on TMP build up.

Conclusions

It is demonstrated in this paper that ozonation/biofiltration is an interesting method for treatment of humic surface water and that the rotating membrane disc biofilm reactor can favorably be used for this process. The following conclusions can be drawn from this paper:

- Ozonation will remove colour in humic water. The typical dosage related to around 80 % colour removal will be 0.15 mg O_3/mg Pt or 1.0-1.5 mg O3/mg $TOC_{raw\ water}$.
- The easily biodegradable ozonation by-products that are formed (carboxylic acids, aldehydes and keto acids) are biodegraded in a biofilter according to first order kinetics.
- The empty bed residence time (EBCT) is more important for the biodegradation in a biofilter that the type of biofilter medium. A typical EBCT of 20 min will be required.
- The biomass production during biodegradation is so small that filter run times in the order of 2-4 weeks are sufficient.
- The rotating membrane disc bioreactor can favorably be used for the ozonation process by carrying out both biodegradation as well as biomass separation in the same reactor. The design flux should probably not exceed 0.5 m/d (20 l/m^2h).
- The use of small sponges to clean the membranes in order to prevent cake layer formation and fouling was shown to be very efficient. More experiments are needed in order to optimize this system and its cleaning procedures.

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