

Treatment of humic surface water at cold temperatures by ozonation and biofiltration

E. Melin*, B. Eikebrokk*, M. Brugger** and H. Ødegaard***

* SINTEF Applied Chemistry, Department of Water and Wastewater, N-7465 Trondheim, Norway

** Hydro-Elektrik GmbH, Ravensburg, Germany

*** Norwegian University of Science and Technology, Department of Hydraulic and Environmental Engineering, Trondheim, Norway

Abstract A small full-scale ozonation/biofiltration plant was operated for 1.5 years in mid-Norway. A three-media biofilter was used to remove biodegradable organic matter from ozonated water. The biofilter contained granular activated carbon (GAC), phonolith and CaCO_3 and was operated at 26–30 min. empty bed contact time. The water temperature varied between 2 and 14°C but the biofilter was operated most of the time at temperatures below 10°C. Total phosphorus concentration in the raw water was also very low (1.1–2.0 $\mu\text{g L}^{-1}$). Batch tests showed that low phosphorus concentration and low temperature are potential limitations for microbial growth and organic carbon removal. Initially, the GAC adsorbed organic carbon while the microbial activity was building up. Most of the adsorption capacity was used after 1.5 months of operation. After this period, 14–33% of the TOC was removed (average 23%). Although the overall TOC removal in the process was modest, average BDOC removal of 55% was observed even at 3°C. Ozonation was effective in reducing colour with average removal of 80%. The results show that significant biological activity can be achieved and maintained in biofilter treating ozonated water even at low temperatures and phosphorus limited conditions.

Keywords Biofiltration; low temperature; ozonation; water treatment

Introduction

In Norway, surface water is the main source of drinking water. The microbial quality and high content of humic substances and colour are the main problems in water treatment. Ozone is a very effective disinfectant and also reacts with humic molecules to reduce the colour. Some of the reaction products are easily biodegradable and must be removed in a biofilter to prevent excessive growth in the distribution net. However, low water temperatures and low nutrient concentrations are potential limitations for biofilter performance in northern climates.

One of the advantages of ozonation/biofiltration is the ease of operation. Ozone is generated in the plant and no use of external chemicals is required if chlorine is not used for final disinfection. Although ozonation/biofiltration is widely used in Central Europe, it is not a common treatment method in Norway. The efficiency of the process for removal of humic substances in pilot-scale has been previously reported (Ødegaard, 1996; Melin and Ødegaard, 1999). To further demonstrate the technology in Norway, a small full-scale treatment plant was tested in the mid-Norway area for treatment of humic surface water. This paper reports results from 1.5 years of operation.

Materials and methods

Figure 1 shows a schematic of the treatment plant. The treatment plant was manufactured and installed by Hydro-Elektrik GmbH (Ravensburg, Germany). The plant was located by Lake Leirsjøen in Trondheim, which represents a typical Norwegian surface water.

The ozone is applied in two stages. The ozone is generated from dried air and mixed with

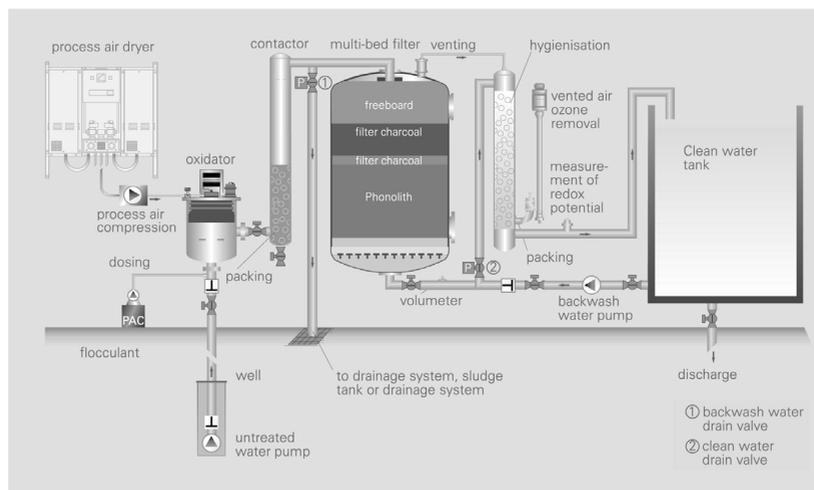


Figure 1 Schematic of the ozonation/biofiltration plant

raw water in an enclosed hydraulic system through a venturi/injector system. After ozone addition, the water flows through a packed contact column (diameter 0.3 m, height 4 m) for colour removal and disinfection. The air with residual ozone is then vented into another contact column (diameter 0.3 m, height 3.5 m), where bacteria present in biofilter effluent are killed (hygienisation).

The biofilter (diameter 1.3 m, height 4 m) was filled with three different media. The upper layer consisted of 0.8 m of granular activated carbon (GAC) with particle size of 0.5–2.5 mm. The GAC removes the residual ozone from the water and acts as a biofilm carrier. In the middle was a 1.1 m layer of volcanic stone phonolith (0.3–0.8 mm). This layer acts as biofilm carrier and particle separation media. Since the surface water in Norway has usually low pH and alkalinity, the filter had an additional layer (0.4 m) of calcium carbonate (1–3 mm) to increase pH, calcium and alkalinity in the water for improved corrosion control. The treatment plant was operated with a flow rate of 6–7 m³ h⁻¹ resulting in empty bed contact times (EBCT) of 26–30 min. and filter velocities of 4.6–5.3 m h⁻¹.

The applied ozone dosage varied between 1 and 2 mgO₃ mgTOC⁻¹ but most of the time was around 1.5 mgO₃ mgTOC⁻¹. The ozone dosage was adjusted to give around 80% removal of colour. Since the ozone generation and mixing with water was done in a closed system, the ozone production could not be measured but was based on calibration done in the factory. It is not known how much of the ozone was transferred into water and how much was lost through the vented air.

The samples were taken from the raw water and the clean water tank if nothing else is indicated. Total organic carbon (TOC) was analysed using a Rosemount Dohrmann DC-190 total organic carbon analyser. Chemical oxygen demand (COD) was analysed by oxidation with permanganate. Colour was measured spectrophotometrically with a Hitachi U-3000 spectrophotometer at 410 nm using potassium chloroplatinate as standard and UV-absorbance was measured at 254 nm with the same instrument. Turbidity was measured using a HACH 2100N Turbidimeter. Alkalinity and pH were analysed using Metrohm Titroprocessor 726 equipped with sample changer 717 and Dosimat 685. Calcium and phosphorus was analysed by inductively coupled plasma mass spectrometer (ICP-MS). Heterotrophic plate counts from the treatment plant were determined using the pour plate technique with peptone-yeast agar and incubating for three days at 20°C. The method was chosen as it is normally used to analyse bacteria in drinking water and in order to compare the results with drinking water standards. Biodegradable dissolved organic

carbon (BDOC) was analysed using method developed by Servais *et al.* (1987). The water sample was filtered through a 0.2 μm filter. Two samples in 40 mL vials were acidified and stored at 4°C. Two other samples were inoculated by bacteria enriched from the biofilter effluent (0.4 mL). TOC was measured after incubation for one month at room temperature and BDOC was the difference between control and incubated samples.

Additional batch tests were carried out to study the effect of nutrients and temperature on microbial growth and TOC degradation. Ozonated water was collected from the free-board into 1 L acid washed bottles. The bottles were inoculated with bacteria from biofilter effluent. One bottle was stored at 4°C after adjusting the pH to 2 to serve as an abiotic control. When nutrients were added, K_2PO_4 was added to give a final phosphorus concentration of 0.1 mg L^{-1} and 1:1.9 (by weight) mixture of NH_4Cl and KNO_3 to give a final nitrogen concentration of 1 mg L^{-1} . The bottles were periodically sampled for TOC and heterotrophic plate counts. The heterotrophic plate counts from batch tests were done by the spread plate method using R2A agar and incubating for seven days at 20°C.

Results and discussion

Table 1 shows the measured parameters in raw water and clean water. The average total organic carbon (TOC) removal was 23% from the raw water. The average removals of colour and UV-absorbance were 79% and 68%, respectively. Turbidity of the raw water was very low and removal was moderate (28%). On average, the CaCO_3 layer increased pH by 0.7 units and alkalinity by 0.33 mmol L^{-1} . The heterotrophic counts in biofilter effluent varied between 4 and over 6000 cfu mL^{-1} but were on average around 150 cfu mL^{-1} . The plate counts were lower than earlier observed from coarser biofilter media in pilot-scale (Melin *et al.*, 2000). The fine phonolith layer may have been effective in retaining bacteria or the low phosphorus content of the water limited microbial growth (see below). After the second ozonation column, the counts were below 1 cfu mL^{-1} if ozone residual in water was at least 0.05 mg L^{-1} . Some growth took place in the clean water tank (Table 1). The measured parameters in treated water comply with Norwegian drinking water standards.

Figure 2 shows the temperature in raw water during the experiments. The water temperature was between 2 and 4°C during winter. During summer, the water reached the highest temperature of 14°C, but the biofilter was operated most of the time at temperatures below 10°C. Figure 3 shows the removal of TOC during the experiments. Initially, the GAC layer adsorbed TOC but the adsorption capacity was used approximately after 1.5 months of operation (this period is excluded from calculations in Table 1). Initial adsorption of TOC into GAC makes it difficult to evaluate when significant biological activity started. There is a small increase in TOC removal after four weeks, which could be due to microbial activity.

Table 1 Minimum, maximum and average values for analysed parameters in raw water and clean water

Parameter	Raw water			Clean water			Average removal (%)
	Min.	Max.	Average	Min.	Max.	Average	
TOC (mg L^{-1})	2.99	4.77	3.72	2.21	3.52	2.85	23.0
COD (mgO L^{-1})	3.52	6.13	4.68	1.44	3.31	2.36	49.9
Colour (mgPt L^{-1})	21.2	33.9	27.0	1.9	9.3	5.7	79.3
UV-abs (E m^{-1})	13.4	20.4	16.3	2.5	7.3	5.3	67.7
Turbidity (NTU)	0.15	0.50	0.27	0.11	0.38	0.18	27.5
pH	6.75	7.52	7.04	7.45	8.15	7.76	NA
Alkalinity (mmol L^{-1})	0.21	0.45	0.37	0.51	0.87	0.70	NA
Calcium (mg L^{-1})	7.33	8.60	7.69	9.66	15.3	13.8	NA
Heterotrophic bacteria (cfu mL^{-1})	NA	NA	NA	<1	33	10	NA
Temperature ($^{\circ}\text{C}$)	1.4	13.6	6.1	NA	NA	NA	NA

NA = not analysed or not applicable

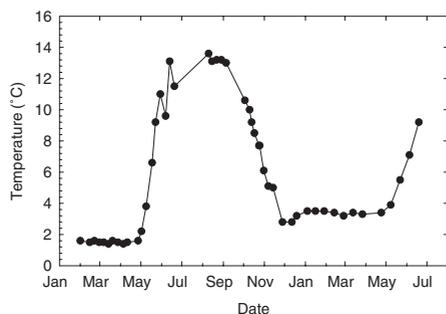


Figure 2 Raw water temperature during the experiments

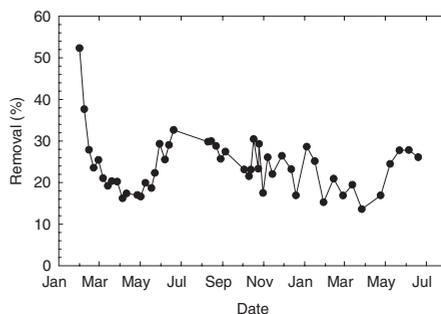


Figure 3 Removal of TOC in the treatment plant

A pilot-scale study at the site showed that TOC removal started after three weeks at 3°C in biofilter containing inert media (results not shown). This is close to the start-up times (20–40 days) observed by Liu *et al.* (2001) for easily biodegradable ozonation by-products at 5°C. The TOC removals are in the same range as observed previously in pilot-scale (Melin and Ødegaard, 1999).

The TOC removal seems to follow seasonal variations with the highest removal during the summer and the lowest in the late winter. The increase in TOC removal in spring occurs about the same time as the temperature starts to increase. However, while temperatures decreased to 3°C at the end of November, the general trend in the TOC removal was a more gradual decrease during the winter. Figure 3 shows the TOC removal as a function of the temperature. The correlation between temperature and TOC removal is not very good ($r^2 = 0.43$), although there is an increasing trend with increasing temperature. Other factors like ozone dosage and changes in water quality might also have influenced biological activity in the biofilter.

Recently, Lehtola *et al.* (2001) have shown that phosphorus can be a growth limiting nutrient in ozonated waters. Several analyses from the raw water showed that the phosphorus concentration was very low. The total phosphorus varied between 1.1 and 2.0 $\mu\text{g L}^{-1}$ and it is difficult to know how much of it was in biologically available form. Figure 5 shows TOC removal as a function of raw water phosphorus concentration. The results are divided into two temperature ranges to screen out the effect of water temperature. The correlation is not very good. Relatively small variations in phosphorus concentration and low number of analyses make the results quite inconclusive. There was no correlation between the applied ozone dosage and TOC removal.

Table 2 shows values for BDOC in the ozonated water and the biofilter effluent. Between October 10–24, different ozone dosages were tested which explains the increase

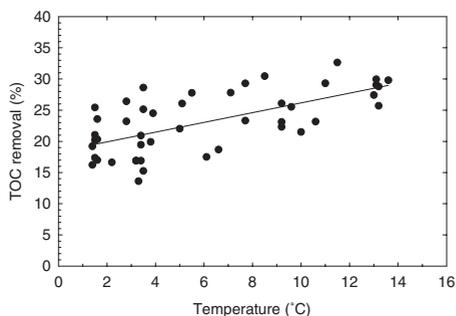


Figure 4 TOC removal as a function of the raw water temperature

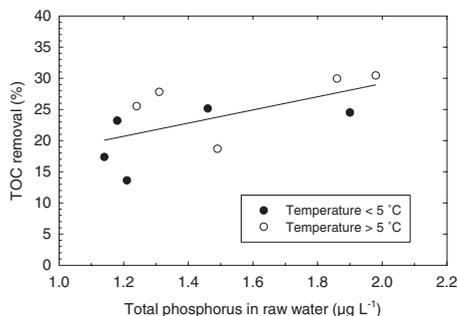


Figure 5 TOC removal as a function of raw water phosphorus concentration

Table 2 Biodegradable organic carbon (BDOC) in ozonated and biofiltered water

Date	Ozonated (mg L ⁻¹)	Biofilter (mg L ⁻¹)	Removal in biofilter (%)	Water temperature (°C)
10 October 2000	0.75	0.48	36	10.0
17 October 2000	0.95	0.30	68	8.5
24 October 2000	1.22	0.47	61	7.7
28 November 2000	1.05	0.36	66	2.8
27 March 2001	1.04	0.60	42	3.3
11 May 2001	1.18	0.48	59	3.9
22 May 2001	1.00	0.48	52	5.5

of BDOC in ozonated water. The BDOC removal was 36–68% (average 55%), but there is no correlation between water temperature and BDOC removal. The results show that there can be significant removal of BDOC even if the water temperature is 3–4°C.

The effect of nutrients and temperature on microbial growth and organic carbon degradation in ozonated water was studied in batch tests. The bottles were inoculated with bacteria enriched from the biofilter effluent. Figure 6 shows the removal of TOC compared to the control and growth of heterotrophic bacteria in ozonated water with no nutrient addition and with phosphorus or phosphorus and nitrogen. The results show that in a batch test, the microbial growth in ozonated water is limited by phosphorus, as also observed by Vartiainen *et al.* (2001). In the bottles containing added phosphorus, the maximum heterotrophic plate counts were ten times higher than without added phosphorus. For comparing the TOC removal rates, the following equation was used:

$$R = R_{\max} (1 - e^{-kt}) \quad (1)$$

where R is the TOC removal (mg L⁻¹), R_{\max} is the maximum TOC removed (mg L⁻¹), k is the removal rate (d⁻¹), and t is time (days). The results are shown in Table 3. Lower growth in the absence of added phosphorus also reduced the rate of carbon removal, which was about four times lower without added nutrients.

When the water for the batch test was taken, no analyses were made from the treatment plant. To compare the batch results with the biofilter performance, the average removal of TOC in the biofilter one week before and after was plotted into Figure 6a (horizontal dashed line). The TOC removal in the biofilter was close to the removal of TOC in the nutrient amended bottles at the time when the maximum plate count was observed. This indicates that the biofilter removed the fraction of the BDOC which supports rapid growth in the batch culture. It also indicates that the TOC degradation in the biofilter was not as limited by phosphorus as the batch test showed. It may be possible that the biofilter reaches

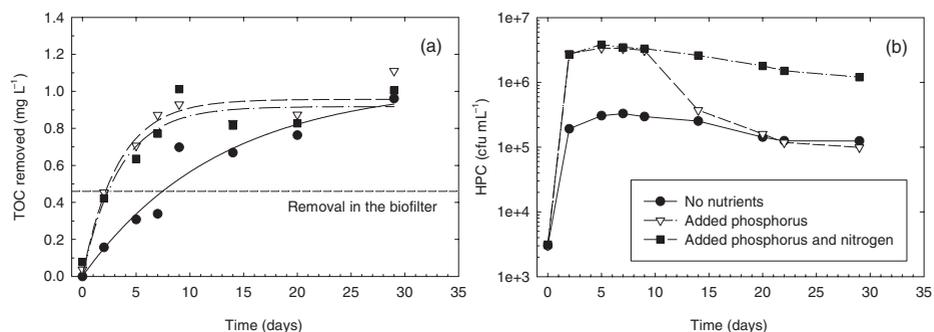


Figure 6 Effect of nutrient addition on degradation of: (a) organic carbon, and (b) microbial growth in batch test at 22°C

Table 3 Rate constants for TOC removal in the batch tests

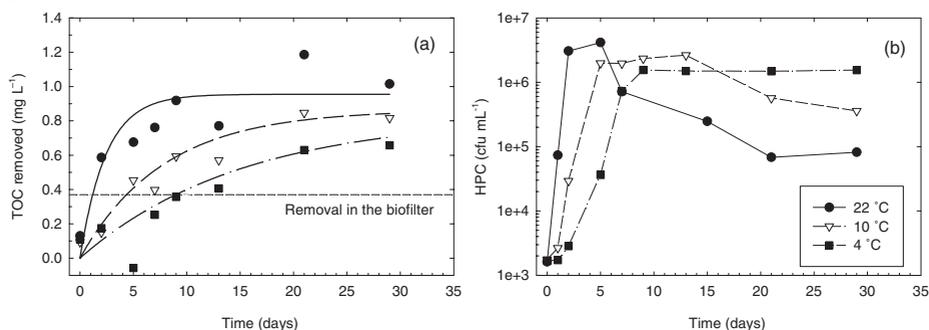
Test	Added nutrients	Temperature (°C)	R_{\max} (mg L ⁻¹)	k (d ⁻¹)	r^2
Nutrient	None	22	1.04	0.079	0.94
	P	22	0.96	0.30	0.94
	P + N	22	0.92	0.29	0.91
Temperature	P + N	4	0.95	0.066	0.93
	P + N	10	0.86	0.13	0.94
	P + N	22	0.83	0.41	0.80

a pseudo steady-state where additional phosphorus becomes available from dead cells that undergo lysis. Vahala *et al.* (1998) compared two GAC filters treating ozonated water. Additional phosphorus was fed into one of the biofilters but there was no difference in removal efficiency between the biofilters. Only the amount of heterotrophic bacteria was higher in the effluent of the nutrient amended biofilter.

The effect of temperature on microbial growth and TOC degradation was also studied in a batch test (Figure 7). Phosphorus and nitrogen was added into bottles to ensure maximal growth rate. At temperatures below 22°C, growth and TOC degradation becomes slower although the effect is not extreme. At 22°C, the maximum growth was observed after 2 days, while at 4°C it took between 7 and 9 days. The reason for rapid decrease in plate counts in some bottles may be due to protozoan activity. Table 3 shows the rates for the TOC removal. The negative value on day 5 at 4°C was omitted from the curve fit. The removal rate was about two times higher at 10°C than at 4°C.

Liu *et al.* (2001) did not observe significant differences in degradation of selected ozonation by-products in biofilters operated at 5°C and 20°C. The reason was that at higher temperatures most of the degradation activity occurred only in the top layers of the filter. At lower temperature, the degradation activity occurred throughout the entire filter. A similar effect might have buffered influence of the temperature also in our experiments, when the temperature decreased after the summer without immediate effect on TOC removal in the biofilter.

The horizontal dashed line in Figure 7a shows the TOC removal in the biofilter one day before the ozonated water was taken for the batch test. In this experiment, the TOC removal in the biofilter and bottles corresponded quite closely with maximum plate counts at 4 and 10°C, although at room temperature the TOC removal was higher. The results indicate that a simple batch test could be used to evaluate the extent of BDOC removal in biofilters by measuring removed TOC when the heterotrophic plate counts reach their maximum. However, this should be studied further with more frequent sampling to optimise incubation temperature and nutrient addition and using samples from several different treatment plants.

**Figure 7** Effect of temperature on degradation of: (a) organic carbon, and (b) microbial growth in batch test at different temperatures

Conclusion

The results show that significant biological activity can be achieved and maintained in biofilter treating ozonated water even at low temperatures and phosphorus limited conditions. There was some seasonal variation in the TOC removal. While increases in temperature in the early summer corresponded with increased TOC removal, the decreasing temperature in autumn did not result in immediate reduction in removal efficiency. Some other changes in water quality might also have affected the removal efficiency. There were not enough results to make conclusions whether or not changes in raw water phosphorus affected the biofilter. Although the overall TOC removal was modest in the process, good colour removal was achieved by ozonation and on average about half of the BDOC was removed.

Acknowledgements

This work was financed by Hydro-Elektrik GmbH and Norwegian Research Council.

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