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Removal of natural organic matter by ultrafiltration and nanofiltration for drinking water production

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Abstract

Water from Lake Butoniga near the town of Buzet, Croatia, was used as a source for drinking water production. Since lake water has a high concentration of trihalomethane precursors, a treatment was necessary. A process including ozonation, flocculation and filtration was chosen on the basis of preliminary work in a trial pilot plant with a capacity of 10 m^3 h^{-1}. Although the chosen process succeeded in producing water that met the demands for drinking water, the efficiency of the removal of natural organic matter was relatively low. Ultrafiltration (UF) and nanofiltration (NF) processes were investigated as alternatives and possible upgrades of the process. Experiments were conducted at pilot plants with the Mavibran SP 006A and Romicon PM 10, PM 50, GM 80 and PM 500 UF membranes as well as with the Filmtec NF 45 NF membrane. Since most of the organic matter in the lake water was smaller than 6–8 kD, the use of the NF process was proposed. To avoid fouling of the NF membrane, we used flocculated and filtrated water from the trial plant as NF feed water. This combination produced water of high quality while process parameters remained stable over the entire period of investigation.

Keywords: Nanofiltration; Ultrafiltration; Natural organic matter; Drinking water

1. Introduction

A part of natural organic matter (NOM) in raw water forms carcinogenic trihalomethane (THM) during the disinfection process. NOM in water may also be responsible for bacterial regrowth in distribution networks. Recently, membrane processes for removal of NOM from surface waters have proven to be efficient and economically acceptable [1], at least in small systems. Ultrafiltration (UF) is efficient in reducing turbidity, particles and suspended solids [2], but it is usually not effective in removal of the humic substances [3], which have the highest potential in NOM for THM formation [4]. Taylor et al. [5] have shown

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nanofiltration (NF) to be very effective in removing THM precursors from high-colour ground water in Florida. They found that reverse osmosis is also highly effective in THM precursor removal, but it requires much higher pressure and produces lower flux. Other authors [6,7] also suggest NF as an efficient and reliable process for NOM removal. The major problem in use of membrane processes for NOM removal is the requirement for pre-treatment in order to prevent fouling of the membrane. Fouling occurs mostly due to colloidal and scale precipitation as well as microbial growth. Several authors have studied mechanisms and prevention from fouling [8–11] and have searched for an optimal type of pre-treatment [12]. The role of hydrodynamic parameters such as initial permeate flux and cross flow velocity is found to be significant as well as the role of complex between divalent cations and NOM. Due to a great complexity of NOM, much is yet to be done. Therefore, the knowledge of organic and inorganic composition of raw water is essential for designing a membrane process.

We studied the potential use and characteristics of UF and NF membranes comparing them with a conventional process based on flocculation, filtration and ozonation with regard to NOM removal.

2. Methods

2.1. Conventional trial plant

The trial plant consisted of pre-ozonation tank, coagulation–flocculation–flotation unit, dual-media filter (DMF), main ozonation and slow sand filter (Fig. 1). Flow rates through the trial plant were 10 $m^3 h^{-1}$ through pre-ozonation and flocculation units, 4–5 $m^3 h^{-1}$ through DMF filter and 2 $m^3 h^{-1}$ through slow sand filter. Surplus water was discharged. The pre-ozonation tank was cylindrical with a volume of 0.416 m^3 and the ozone dose was 0.5–2.1 mg dm^{-3}, depending on feed water turbidity as well as organic matter and manganese concentrations. The coagulation–flocculation–flotation unit consisted of five chambers, the first of which served for coagulation, the second and third for mixed flocculation, the fourth for non-mixed flocculation and the fifth for air enhanced flotation. Volumes of the chambers were 0.26, 0.85, 0.85, 0.26, 2.63 m^3, respectively. The process in chambers was induced with PAC 200–Alpoclar coagulant $[Al(OH)_a(Cl)_b(SO_4)_c]$ with an average dose of 1.5 mg/L and sulphuric acid for pH balance between 6.4–7.7. The DMF filter was a cylinder (d = 0.8 m; h = 4.5 m) filled with 60 cm of sand (mesh 0.3–0.8 mm) and 80 cm of Aquafilt pumice (mesh 0.8–1.5 mm). A dual-media filter was automatically cleaned with backwash whenever the pressure drop increased, which occurred in 24- to 48-h intervals. The main ozonation was performed in three 0.34 m^3 chambers, with the ozone dosed in the first two. The dose was set in order to obtain 0.1–0.2 mg dm^{-3} of residual ozone after the third chamber. Final slow sand filter (mesh 0.25–0.3) with a volume of 16.2 m^3 and a linear filtration velocity of 0.3 m h^{-1} served for the final reduction of organic matter and maintaining the water quality.

2.2. Membranes and membrane testing units

Hollow-fibre Romicon PM 10, PM 50, GM 80 and PM 500 membranes (molecular weight cut-offs (MWCO): 10, 50, 80 and 100 kD, respectively), with 57-cm long and 2-mm wide fibres in a 5-cm diameter pressure vessel were used for the UF experiments. A spiral-wound SP-006-A Mavibran membrane (polyether sulphone with a MWCO of 6–8 kD) was also used for UF experiments. A Filmtec NF 45 spiral-wound membrane with a thin-film composite layer (MWCO 300 D) was used for the NF experiments. The Romicon membranes had already been used several times for filtration of surface waters while the other membranes were new. All membranes were pre-cleaned with an alkaline solution before the experiments began.

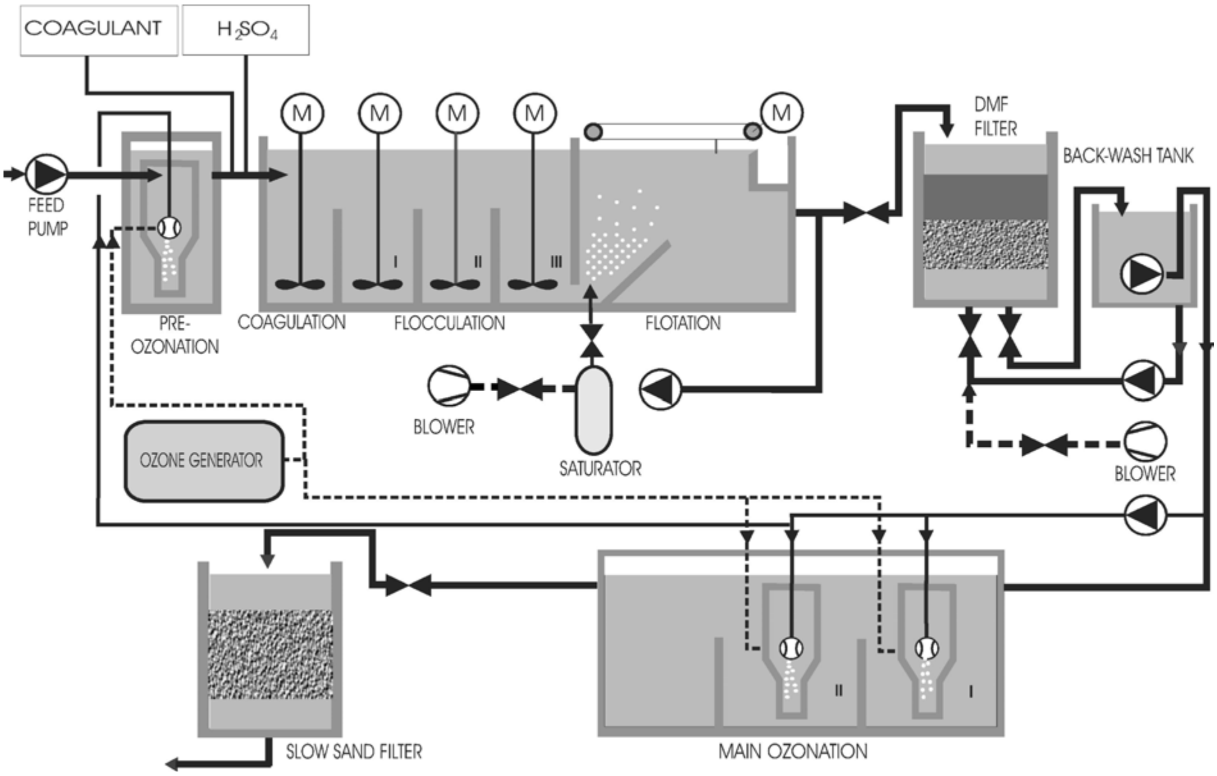

Fig. 1. Scheme of conventional trial plant.

Three pilot plants for membrane testing were used. All modules consisted of pressure pumps; pressure vessels housing the membrane; and associated pressure gauges, valves and flow meters. Only the NF module had a cartridge filter (5-µm pore size) preceding the NF membrane. All three pilot plants were used for filtration of original lake water taken from a depth of 4 m, while the NF pilot plant solely filtered water taken after the DMF filter from a conventional pilot plant continuously over a 3-month period at 75% water recovery.

2.3. Analyses

Samples of feed water and samples of water at several stages of the conventional process were taken as well as permeate and concentrate from membrane filtration pilot plants. Analyses based on standard methods were pH, conductivity, total dissolved solids, turbidity (HACH 1720 C turbid meter), TOC (Shimadzu TOC 5050A), permanganate oxygen demand, alkalinity, total hardness as well as iron, manganese and ammonium concentrations.

3. Results and discussion

Lake Butoniga is an artificial water resource with an area of 2.5 km^2 and an average depth of 7 m with a volume of approximately 20 Mm^3. It is located near the city of Buzet, Croatia, and its purpose is to ensure enough potable water for the Istria Peninsula. According to Croatian regulations, a pre-treatment is necessary since water from the lake fails to meet maximum contaminant

Table 1
Concentrations of pollutants in water from Lake Butoniga (April–August, 2000) and their MCL according to Croatian regulations

	Average	Minimum	Maximum	MCL
Iron, mg/l^{-1}	0.087	0	0.342	0.3
Manganese, mg/l^{-1}	0.185	0	0.727	0.05
Ammonium, mg/l^{-1}	0.163	0	1.355	0.14
Turbidity, NTU	4.497	1.028	19.652	4.0
$KMnO_4$ consumption, mg O_2 l^{-1}	2.53	1.61	3.88	3
TOC, mg/l^{-1}	2.75	2.10	4.03	—

levels (MCL) for several pollutants. As can be seen from the contaminant concentrations listed in Table 1, the main problem is organic matter that often exceeds MCL, as $KMnO_4$ consumption, which causes high turbidity and generates high ammonium concentration due to its decomposition. There are also problems with iron and manganese concentrations.

In order to remove pollutants, a process that includes flocculation, filtration and ozonation was designed and a trial pilot plant with capacity of 10 m^3 h^{-1} was built for preliminary investigation. On the basis of this investigation, a full-scale plant with a 85,000 m^3/d capacity is now under construction.

The trial plant succeeded in removing iron and manganese beyond detection levels by ozone oxidation and filtration of their oxides. It also removed ammonium by nitrification. However, the designed process was not so efficient in organic matter removal. As shown in Fig. 2, turbidity was reduced almost completely after the first DMF filtration, but organic matter as TOC was reduced by less than 50%. Due to ozone disinfection, there was no formation of THM. Also total organic matter was below MCL, but its concentration was relatively high.

During the testing period, the effect of pre-ozonation on NOM removal was observed. The removal of UV-254 absorbing NOM was increased from 70 to 85% when the pre-ozonation

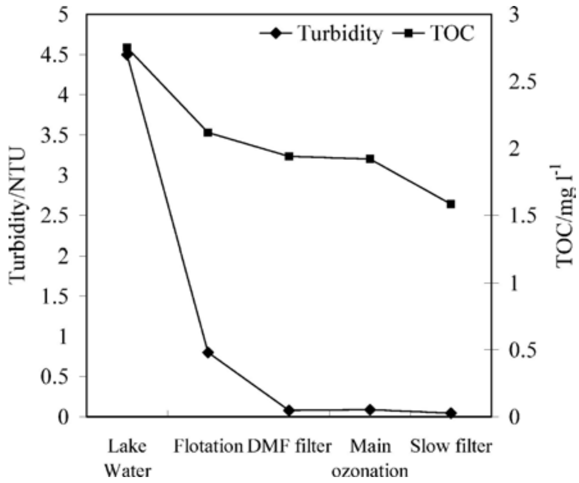

Fig. 2. Turbidity and TOC at different stages of treatment with the conventional trial plant.

dose was increased from 0.5 to 1.2 mg O_3/L. There was no significant increase of the NOM removal with the applied doses over 1.2 mg O_3/L. This probably occurred due to a partial oxidation of UV-254 absorbing substances as well as micro-flocculation of humic substances, which led to better removal efficiency in the flocculation stage.

As stated previously [1], membrane processes are more efficient in removal of NOM from water than the conventional flocculation process. The performance of UF and NF membranes was tested in the treatment of the lake water in order

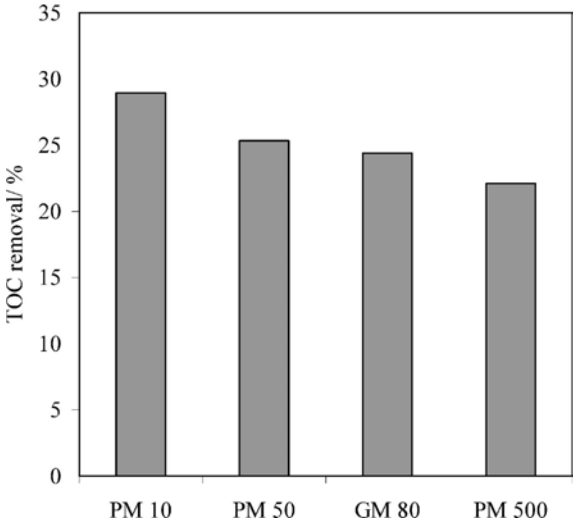

Fig. 3. TOC removal with Romicon hollow-fibre membranes with feed lake water.

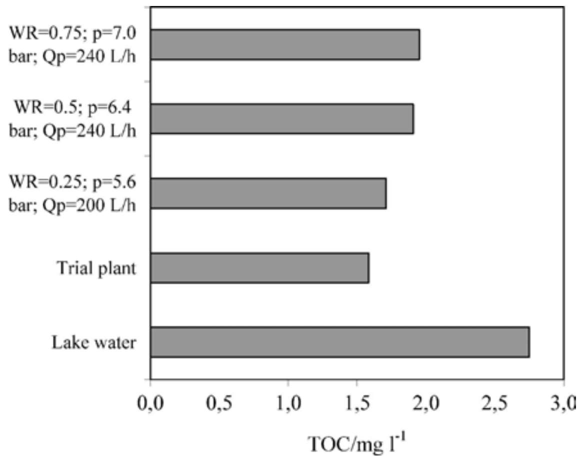

Fig. 4. TOC in lake water, water treated at a conventional trial plant and with the Mavibran UF membrane at different water recoveries (WR).

to investigate a possible future upgrade of the treatment plant.

Romicon UF hollow-fibre membranes showed only partial rejection of TOC (Fig. 3), leading to the conclusion that most of the organic matter was smaller than 10 kD, which was the nominal cut-off of the PM 10 membrane. Since PM 500, with the nominal cut-off of 500 kD, removed 22% of the present organic matter, it can also be stated that significant part of the NOM from the lake water was larger than 500 kD. Differentiation of NOM by UF with different molecular weight cut-offs was performed by Ratnaawera et al. [13] by measuring UV-absorbance (254 nm) of the collected fractions. A detailed determination of NOM molecular weight was investigated by Egeberg et al. [14] with UF as a method with a similar experimental set-up as in the present work. Their experiments showed that the choice of membrane could seriously affect determination.

A Mavibran SP 006A spiral-wound membrane with nominal cut-off of 6 kD at different pressures and recoveries showed a rejection similar to the Romicon membranes (Fig. 4), suggesting that it was necessary to employ membranes with smaller cut-offs. Clearly, UF membranes could not be used to upgrade the conventional process, which achieves similar or better NOM removal efficiency itself. Several authors [15,16] have shown that rejection of organics by UF can be increased by the addition of coagulant in the feed water. In the case of the Butoniga waterworks where a full-scale conventional plant shall have sufficient capacity, a membrane stage should be placed as the final one in order to improve water quality and minimize fouling since none of the UF membranes used were suitable for that.

The Filmtec NF 45 membrane was chosen for its relatively low salt rejection to avoid a potential need for re-mineralization of the treated water. As shown in Fig. 5, NF 45 spiral-wound membrane successfully removed more than 80% of NOM at all the conditions studied, showing superior water quality compared to the water produced at the conventional trial plant. The main objective in applying the NF process as a final step in surface water treatment is the removal of NOM and bacteria in order to reduce post-disinfection and bacterial regrowth in the distribution network. Likanen et al. [17] found NF permeates of various

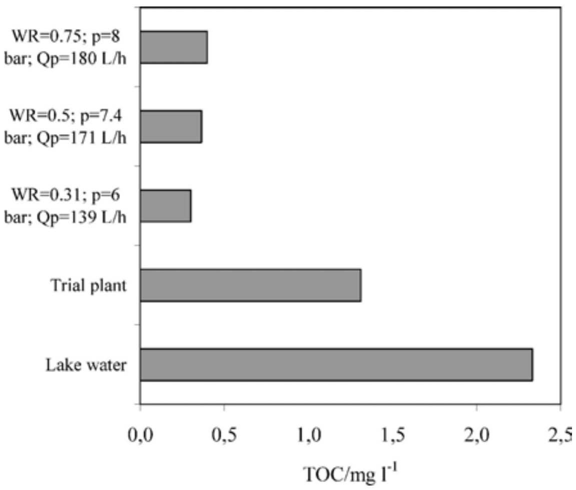

Fig. 5. TOC in lake water, water treated at a conventional trial plant and with a Filmtec NF membrane at different water recoveries (WR) for feed lake water.

membranes biologically unstable and suggested that post-disinfection was necessary in all cases. They also stated that residual organic matter in NF permeate is easily biodegradable, making post-disinfection obligatory.

The salt rejection of the NF membrane was relatively small (Fig. 6) so there was no need for re-mineralization as with reverse osmosis or with NF membranes with higher salt rejections. NF 45 chemically treated water or NF permeate from a membrane with high inorganic removal have low alkalinity, pH and hardness, which leads to chemical post-treatment to prevent corrosion of the water network. Corrosion in the network is usually predicted by monitoring the Langelier Saturation Index (LSI). Since lake water had relatively low total hardness (Fig. 6), its LSI was small (Table 2), indicating under-saturation with $CaCO_3$. This indicates a significant influence of the surface and rainfall on water composition since groundwaters of the area are generally much harder. Water produced by conventional plant also had very low LSI indices (data not shown), which originated from acidification in the flocculation stage. Therefore, it is clear that

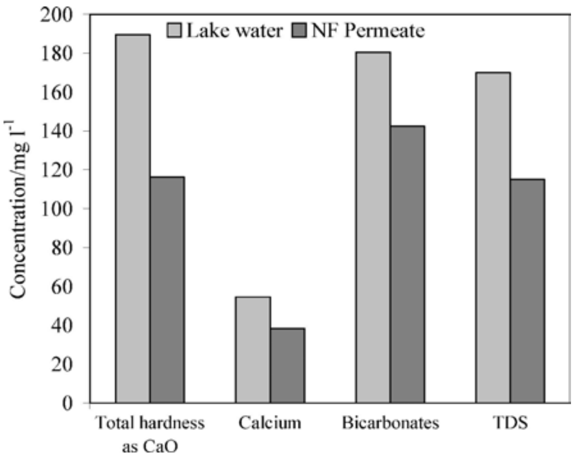

Fig. 6. Concentration of inorganic salts in lake water and NF permeate at $Y = 0.75$ for feed water taken after DMF filtration.

Table 2
Langelier indices for lake water, water taken after DMF filtration and nanofiltration concentrate at different water recoveries, *Y*) when feed water for the nanofiltration was taken after DMF filtration

	Langelier index
Lake water	−0.12
Water filtered through DFM	−0.39
Concentrate:	
Y = 0.25	−0.21
Y = 0.5	−0.11
Y = 0.75	−0.17

NF permeate, produced from water from the conventional plant, would need chemical post-treatment with lime in order to achieve saturation with $CaCO_3$ and prevent corrosion. On the other hand, even the concentrate with the highest salt content was stable towards scale precipitation, making the NF process completely safe from scale fouling. This eliminates pH control by acidification and often complex monitoring [18] of scale formation.

Yeh et al. [19] made a comparison between the conventional coagulation/filtration process

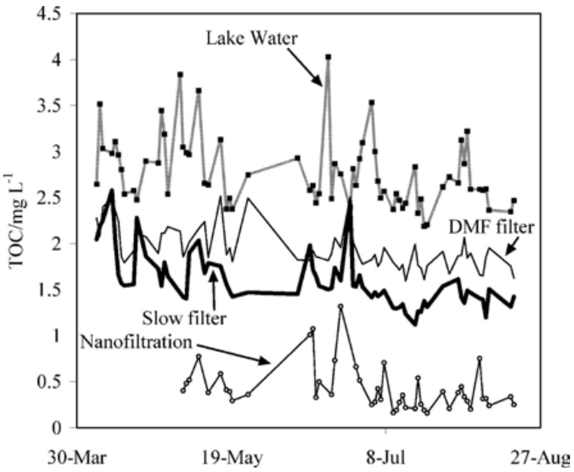

Fig. 7. Comparison of TOC in water treated at a conventional trial plant and in NF permeate when feed water for NF was taken after DMF filtration.

with chlorine disinfection, an alternative process with ozonation and a membrane system with UF and NF. All water quality parameters were significantly improved with membrane processes installed after conventional treatment. The water quality in their work was somewhat better than in the present work since they used a high rejection membrane, the Filmtec NF 70. In such cases problems with scale fouling of membrane and corrosion induced by product water may occur.

At any rate the NF process should be carefully designed with regard to required pre-treatment to prevent biofouling [11]. As the silt density index of lake water was much higher than the suggested maximum value of 3 [6], it was clear that the removal of colloidal particles and turbidity was necessary prior to membrane filtration. Therefore, we used water after DMF filtration from the conventional pilot plant as feed water for the NF process to avoid fouling. Fig. 7 shows the concentration of organic matter in different stages of the process during 3 months of investigation, and it is clear that the NF process produced water of better quality than the conventional trial plant with regard to NOM removal. There was no flux decrease during the entire period, probably due to adequate pre-treatment [11]. However, periodical cleaning might be necessary over extended periods of continuous work.

A similar process design to the one proposed here with an extensive pre-treatment for the NF stage has been applied in full scale (140,000 m^3/h, 37 mgd) in Paris, France [20] for the treatment of river water with low inorganic rejection membranes. Even larger facilities (40 mgd) in Florida [21] are intended to operate a NF plant with minor pH correction, dual-media filters without coagulation and 5-micron cartridge filters for pretreatment. Evidently, NF technology in drinking water production has a stable position both for new treatment plants as well as an upgrade of conventional processes.

4. Conclusions

The results show that the NF process, rather than UF, should be used for the removal of NOM from lake water or to improve the quality of conventionally treated water because most of the organic molecules had relatively low molecular weight and cannot be separated by UF. It can also be stated that conventional flocculation/filtration process can be upgraded successfully with the NF process to achieve better water quality by NF and to minimize organic fouling of NF with conventional water pre-treatment, thus complementing the two processes. The NF membrane with low inorganic rejection showed very good removal of NOM with negligible tendency toward scale fouling.

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