10 Years of Applied Research to Optimize Pre-Treatment and Post-Treatment of the MP UV/H\textsubscript{2}O\textsubscript{2} Process at Water Treatment Plant Andijk

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ABSTRACT
Requirements of a treatment process for drinking water production from challenged surface water sources shifted over the past decades. The role UV can play in an integrated treatment approach is illustrated by a case study discussing the various research results leading to treatment upgrades at Andijk. The paper describes the feasibility of advanced oxidation based on MP UV/H\textsubscript{2}O\textsubscript{2} treatment for organic contaminant control and a robust primary disinfection. The impact of conventional surface water treatment based on coagulation, sedimentation, filtration and advanced surface water pre-treatment, based on ion exchange and ceramic microfiltration, on the efficiency and by-product formation is presented. Finally, the role of post-treatment by biologically activated carbon filtration on by-product and toxicity control is evaluated.

INTRODUCTION
Water treatment plant (wtp) Andijk (The Netherlands) was constructed in 1968 as a conventional surface water treatment plant based on breakpoint chlorination and coagulation sedimentation and filtration (CSF), servicing water from the IJssel Lake as raw water source. Before 1978, the treatment process was upgraded by implementation of granular activated carbon (GAC) filtration (Figure 1). Customer complaints regarding taste and odor were the main cause for this modification. In addition, to further improve the taste and odor of the produced water, post-chlorination was replaced with chlorine dioxide dosage.

The next retrofit of wtp Andijk was necessary in view of upcoming regulations regarding THMs (Kamp et al, 1997). Furthermore, additional disinfection capacity for protozoa was required. Finally, PWN pursued implementation of a non-selective barrier against organic contaminants because of a shift from non-polar to more polar compounds and from just pesticides to a wide variety of micro-pollutants.

Concentrations of organic micro-pollutants such as pesticides, endocrine disruptors and pharmaceuticals as high as 1.0 mg/L have been observed in the raw water source. Storage in reservoirs lowered the maximum concentrations to 0.5 mg/L. Treatment should be capable of lowering this concentration by 80 percent to satisfy the EC standard for pesticides of 0.1 mg/L.

As a non-selective barrier, advanced oxidation was pursued. Initially O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2} treatment was considered (Kruithof et al, 1995). O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2} treatment (O\textsubscript{3}/DOC 1.1 g/g, H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} 2 g/g) proved to be a very robust barrier against organic micro-pollutants. With bromide levels of 300 - 500 mg/L, IJssel Lake water can be regarded as bromide rich. This high bromide content may cause bromate formation by ozone-based processes (Gunten, von, Hoigné, 1994). In CSF pre-treated IJssel Lake water the bromate formation proved to be very high, especially at low water

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**Figure 1:** Treatment process scheme wtp Andijk after implementation of granular activated carbon (GAC) filtration as post-treatment in 1978
temperatures. By increasing the $\text{H}_2\text{O}_2/\text{O}_3$ ratio from 2 to 4 g/g and increasing the pH from 8.0 to 8.3, bromate formation was restricted but could not be lowered to values less than 3 μg/L. Therefore PWN decided to reject $\text{O}_3/\text{H}_2\text{O}_2$ treatment for full-scale application.

Because $\text{O}_3/\text{H}_2\text{O}_2$ treatment achieved the required degradation of organic micro-pollutants, an obvious option was to pursue another advanced oxidation process without the formation of any bromate. For this purpose UV/$\text{H}_2\text{O}_2$ treatment was selected. In the UV/$\text{H}_2\text{O}_2$ application, OH radicals are generated by UV photolysis of $\text{H}_2\text{O}_2$. UV/$\text{H}_2\text{O}_2$ treatment is based on hydroxyl-radical oxidation combined with UV photolysis (Bolton and Cater, 1994). Depending on the chemical characteristic of the pollutant, one of these two processes plays a predominant role. Extensive pilot and bench scale work at PWN showed that UV/$\text{H}_2\text{O}_2$ treatment met all criteria for disinfection, organic contaminant control without the formation of THMs and bromate. Besides, no formation of harmful metabolites from the priority compounds was observed.

In 2004 at wtp Andijk breakpoint chlorination was stopped and the MP UV/$\text{H}_2\text{O}_2$ installation was located after the existing CSF pretreatment (Figure 2). The MP UV/$\text{H}_2\text{O}_2$ is followed by GAC filtration and by chlorine dioxide post disinfection. The MP UV/$\text{H}_2\text{O}_2$ installation consists of three independent process lines with four UV reactors each. Per UV-reactor 16 MP UV-lamps of 12 kW are installed.

**PRACTICAL EXPERIENCES WITH MP UV/$\text{H}_2\text{O}_2$ TREATMENT USING NATURAL QUARTZ SLEEVES OF CSF PRE-TREATED WATER**

**Disinfection**

Primary disinfection with breakpoint chlorination proved to be an insufficient barrier against protozoa. Bench and pilot scale research into the inactivation of pathogenic organisms by UV, resulted in dose response relationships for MS-2 phages, Bacillus subtilis spore, Giardia muris and Cryptosporidium parvum (Kruithof and Kamp, 2005). It was observed that no reactivation of encysted protozoans was observed at UV-doses > 60 mJ/cm$^2$ (Belosevic et al, 2001). Collimated beam experiments showed that the required 3 log inactivation of Cryptosporidium parvum was obtained at doses lower than 120 mJ/cm$^2$ (Figure 3).

In 2004 at wtp Andijk breakpoint chlorination was stopped and the MP UV/$\text{H}_2\text{O}_2$ installation was located after the existing CSF pretreatment (Figure 2). The MP UV/$\text{H}_2\text{O}_2$ is followed by GAC filtration and by chlorine dioxide post disinfection. The MP UV/$\text{H}_2\text{O}_2$ installation consists of three independent process lines with four UV reactors each. Per UV-reactor 16 MP UV-lamps of 12 kW are installed.

**Organic Micro-pollutant Control**

As an alternative for $\text{O}_3/\text{H}_2\text{O}_2$ treatment the feasibility of UV/$\text{H}_2\text{O}_2$ treatment was studied. During the research period, the scope broadened from pesticides to pharmaceuticals, endocrine disrupting compounds, solvents and algae toxins. In bench scale experiments dose-response relationships have been established for these organic pollutants (Kruithof and Kamp, 2005).

Inactivation of Cryptosporidium parvum oocysts was studied on pilot scale as well. The results showed that on pilot scale the same inactivation could be achieved as in the collimated beam experiments (Figure 3). From the good agreement between the results of the collimated beam experiments and the pilot experiments it was concluded that UV disinfection was feasible for primary disinfection of surface water. The required UV-dose for primary disinfection for the wtp Andijk situation was 120 mJ/cm$^2$, while the standard UV dose for AOP conditions was 540 mJ/cm$^2$, resulting in a superior disinfection.

**Reference compounds atrazine and bromacil, were reduced by 80 percent and 70 percent respectively at process conditions 0.54 kWh/m$^3$ and 6 mg/L $\text{H}_2\text{O}_2$. Figure 4 shows the electrical energy per order (EE/O) for atrazine and bromacil degradation in CSF pre-treated IJssel lake water with a relative low UVT and an average nitrate concentration.** For compounds such as carbamazepine, diclofenac, bisphenol A, microcystine, 80-100% degradation was observed under the same process.
conditions. A somewhat lower degradation was found for diglyme and ibuprofen while TCA was degraded poorly and PFOA and PFOS were not degraded at all by the UV/H$_2$O$_2$ process. Post treatment by GAC filtration removed the non-oxidizable compounds such as PFOA and PFOS, showing the robustness of a multi-barrier approach based on UV/H$_2$O$_2$ treatment and GAC filtration.

**POST TREATMENT BY GAC FILTRATION**

**Excess H$_2$O$_2$ removal**

For the formation of OH-radicals by the UV/H$_2$O$_2$ process, a large excess of H$_2$O$_2$ is necessary. PWN standard process conditions require a H$_2$O$_2$ dose of 6 mg/L (Kruithof and Kamp, 2005). The residual H$_2$O$_2$ is catalytically decomposed completely by GAC filtration, in the first eight minutes EBCT (total EBCT 25 minutes) (Figure 6).

**Biostability**

Advanced oxidation converts trace organic contaminants into biodegradable reaction products when appropriate process conditions are applied. Extensive research efforts in this field did not show any harmful metabolite formation from the converted trace chemical contaminants under those conditions.

**Figure 4:** Electrical Energy per Order for atrazine and bromacil degradation in CSF pretreated IJssel Lake water with a UVT254 84% and 4.7 mg NO3/L and 5 mg H2O2/L

**Figure 5:** MP UV/H2O2 installation at wtp Andijk, PWN Water Supply Company North Holland in The Netherlands

The full-scale UV/H$_2$O$_2$ system for wtp Andijk was designed with an electric energy of 0.54 kWh/m$^3$ for treatment of 3000 m$^3$/h. In a site acceptance test, degradation of atrazine was measured at several UV-doses at a fixed H$_2$O$_2$ dose of 6 mg/L. The installation performed as predicted by the collimated beam experiments and the design models, so design criteria were met. Three streets of four Trojan Swift 16L30 reactors are in operation since October 2004 providing primary disinfection and a barrier for organic contaminants (Figure 5).

**Figure 6:** H$_2$O$_2$ consumption by MP UV/H$_2$O$_2$ treatment and decomposition by GAC filtration

**Figure 7:** Assimilable organic carbon content before and after MP UV/H$_2$O$_2$ treatment and after GAC post filtration of CSF pretreated IJssel Lake water
Advanced oxidation processes such as UV/H$_2$O$_2$ generate biodegradable organic acids from the organic micro-pollutants and especially from natural organic matter (NOM). Assimilable organic carbon (AOC) is a major parameter indicating the biological stability of water (Kooij, van der, et al, 1982). Post filtration by BAC filters lowered the formed AOC content to levels guaranteeing biological stability (Figure 7).

**Nitrite formation and removal**
Nitrite formation by MP UV photolysis of nitrate can be significant. Figure 8 presents the nitrite levels in the full-scale process at wtp Andijk. As expected the nitrite content increased significantly by medium-pressure UV. After MP UV/H$_2$O$_2$ treatment, with natural quartz sleeves, of CSF pretreated water, the nitrite concentration was about 200 mg NO$_2$/L. The formed nitrite is completely re-oxidized to nitrate by post BAC filtration.

![Figure 8: Nitrite formation in CSF and IX-MF pre-treated IJssel Lake water by MP UV/H$_2$O$_2$ treatment utilizing synthetic and natural quartz sleeves](image)

**Formation and removal of genotoxic compounds**
Genotoxicity formation was studied by the standard Amestest. Applying MP UV/H$_2$O$_2$ treatment, utilizing natural quartz sleeves, to the CSF pretreated water, no response was found.

**Summary**
Due to 10 years of applied research the start-up in 2004 and the resulting performance of wtp Andijk has met all treatment objectives: no THMs or other harmful disinfection by-products were formed, robust disinfection was achieved and a non-selective barrier for organic micro-pollutants in an integrated treatment approach of MP UV/H$_2$O$_2$ treatment with post-BAC filtration was achieved. The excess H$_2$O$_2$ biodegradable compounds and nitrite were removed by BAC filtration. The only concern was the substantial energy demand of this MP UV/H$_2$O$_2$ process.

**PRACTICAL EXPERIENCES OF CSF PRE-TREATED WATER WITH MP UV/H$_2$O$_2$ TREATMENT USING SYNTHETIC QUARTZ SLEEVES**
In the UV reactor, the UV-lamps are housed in so-called quartz sleeves, protecting the lamps from direct contact with water and providing thermal insulation for the lamps. Different types of quartz can be applied, some blocking wavelengths <240 nm emitted from MP UV-lamps, others enabling transmission at these wavelengths.

Application of the more transmissive quartz, often referred to as synthetic quartz, allows the transmission of wavelengths <240 nm, contributing strongly to the formation of OH radicals from H$_2$O$_2$. Therefore application of synthetic quartz sleeves results in a lower energy consumption to meet the same treatment objective.

The UV/H$_2$O$_2$ treatment is based on the formation of OH radicals by H$_2$O$_2$ photolysis. The molar absorption of H$_2$O$_2$ increases with lower wavelengths (see Table 1), indicating an economic benefit in utilizing these wavelengths emitted by MP UV. However, as a consequence of the increased availability of photons at lower wavelengths, nitrate photolysis increases as well, resulting in elevated nitrite formation (see Figure 8). Replacing natural quartz sleeves with synthetic quartz sleeves caused an increase in the nitrite formation from 200 mg NO$_2$/L to 600 mg NO$_2$/L.

![Figure 9: Amestest response before and after full-scale MP UV/H$_2$O$_2$ treatment utilizing synthetic quartz sleeves and after post-BAC filtration](image)
the Amestest (see Figure 9). The practical implications of these findings are that additional treatment is required to control these side effects. Currently at PWN, biologically active GAC filters (BAC) following MP UV/H₂O₂ treatment lowers both the genotoxic response and the nitrite concentration (see Figure 8).

**Summary**

By the use of synthetic quartz sleeves, the energy consumption was reduced by about 20 percent. As a disadvantage a significant formation of genotoxic compounds and nitrite by MP UV/H₂O₂ treatment was observed. However, the genotoxic response and nitrite were removed by the post BAC filtration, making this last step an essential part of the treatment. Although synthetic sleeves reduced the required energy, improved pretreatment may bring further energy savings and other benefits.

**PERSPECTIVE: REPLACEMENT OF CSF PRE-TREATMENT BY IX-MF PRE-TREATMENT FOR A RESTRICTED ENERGY CONSUMPTION AND BY-PRODUCT CONTROL**

The energy consumption is strongly dependent on the UV-transmittance of the water. Therefore the composition of the UV absorbing compounds in raw and pre-treated IJssel Lake water was analyzed. The most important UV absorbing compounds in raw IJssel Lake water were found to be NOM and nitrate (Figure 10). The NOM content is rather stable over the year (6.0 mg/L C) while there is a strong seasonal variation of the nitrate content (1-14 mg/L nitrate) with an average concentration of 6.5 mg NO₃/L. To improve the economics of the UV/H₂O₂ treatment, both NOM measured as DOC and nitrate content should be lowered. In the current situation at wtp Andijk, conventional pre-treatment by coagulation, sedimentation and filtration (CSF) is applied. CSF lowers the DOC from 6.0 mg/L to 4.2 mg/L. Nitrate removal by CSF is insignificant. In the near future, PWN will replace the existing conventional pretreatment by ion exchange in combination with ceramic microfiltration (IX-MF).

Pretreatment impacts the composition of the water matrix. CSF lowers the DOC content, but does not impact the nitrate concentration. Advanced pretreatment with ion exchange and ceramic microfiltration (IX-MF) removes both nitrate and DOC (Galjaard et al, 2005). The higher removal of DOC lowers the UV transmission, favoring the formation of OH radicals by UV photolysis of H₂O₂ and lowers the scavenging of OH radicals. The removal nitrate also lowers the UV transmission, favoring once again OH-radical formation.

Compared to CSF, pretreatment by ion exchange improves the DOC removal and even more significantly the nitrate removal. This improved the energy consumption for MP UV/H₂O₂ treatment strongly. Applying IX-MF instead of CSF increased the photon flow absorbed by H₂O₂ by a factor of almost 3 (Table 1). In addition the scavenging of OH radicals was reduced (Martijn et al, 2010).

**Table 1: absorbed photons at wavelengths of 254 nm and 240 nm by 6 mg/L H₂O₂ in several water types**

<table>
<thead>
<tr>
<th>water type</th>
<th>254 nm</th>
<th>240 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw water</td>
<td>2.6%</td>
<td>4.5%</td>
</tr>
<tr>
<td>CSF pretreated water</td>
<td>5.3%</td>
<td>8.2%</td>
</tr>
<tr>
<td>IX-MF pretreated water</td>
<td>14.7%</td>
<td>19.4%</td>
</tr>
</tbody>
</table>

Figure 10: Average annual DOC and nitrate concentration in raw water, CSF pretreated water and IX-MF pretreated water.

Figure 11: EE/O for atrazine and bromacil degradation in CSF pre-treated IJssel Lake water with a UVT₂₅⁴ 84% and 4.7 mg NO₃/L and in IX-MF pre-treated IJssel Lake water with a UVT₂₅⁴ 95% and 2.3 mg NO₃/L and 5 mg H₂O₂/L.
Pilot experiments with MP UV/H\textsubscript{2}O\textsubscript{2} on CSF pretreated water and IX-MF pretreated water were conducted to determine the impact of the pretreatment on the EE/O for reference compounds atrazine and bromacil. The improved removal of DOC and nitrate from the IJssel Lake water by IX-MF pretreatment resulted in a substantially reduced EE/O. Compared to CSF, the EE/O for IX-MF pre-treated water was reduced by about 50 percent (Figure 11).

**By-product control**

Formation of by-products after MP UV/H\textsubscript{2}O\textsubscript{2} treatment of IX-MF pretreated surface water was determined for the parameters; AOC, nitrite and Amestest response. AOC formation was not significantly different from values found after MP UV/H\textsubscript{2}O\textsubscript{2} treatment of conventionally pretreated surface water, despite the lower DOC content. Lower nitrate concentrations after IX-MF pretreatment, resulted in a reduced nitrite formation. Also the Amestest response after MP UV/H\textsubscript{2}O\textsubscript{2} treatment was reduced substantially as a result of improved pretreatment by ion exchange and ceramic microfiltration. However, a small but significant effect of MP UV/H\textsubscript{2}O\textsubscript{2} treatment on the Amestest response remained (Figure 12).

After the last innovation, MP UV/H\textsubscript{2}O\textsubscript{2} treatment is still an essential process for organic contaminant control and primary disinfection in a multi-barrier approach. The economics have improved significantly while the by-product formation was reduced strongly.

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